



## Gas phase precursors to anthropogenic secondary organic aerosol: detailed observations of 1,3,5-trimethylbenzene photooxidation

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K. P. Wyche, P. S. Monks, A. M. Ellis, R. L. Cordell, A. E. Parker, et al.. Gas phase precursors to anthropogenic secondary organic aerosol: detailed observations of 1,3,5-trimethylbenzene photooxidation. Atmospheric Chemistry and Physics Discussions, 2008, 8 (3), pp.11685-11754. hal-00304262

**HAL Id: hal-00304262**

**<https://hal.science/hal-00304262>**

Submitted on 13 Jun 2008

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# Gas phase precursors to anthropogenic secondary organic aerosol: detailed observations of 1,3,5-trimethylbenzene photooxidation

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Received: 15 April 2008 – Accepted: 13 May 2008 – Published: 13 June 2008

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Published by Copernicus Publications on behalf of the European Geosciences Union.

ACPD

8, 11685–11754, 2008

SOA Formation from  
1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Abstract

A series of photooxidation experiments were conducted in an atmospheric simulation chamber in order to investigate the secondary organic aerosol (SOA) formed from the anthropogenic model gas phase precursor, 1,3,5-trimethylbenzene. Alongside specific aerosol measurements, comprehensive gas phase measurements, primarily by chemical ionisation reaction time-of-flight mass spectrometry (CIR-TOF-MS), were carried out to provide detailed insight into the composition and behaviour of the organic components of the gas phase matrix during SOA formation. An array of gas phase organic compounds was measured during the oxidation process, including several previously unmeasured primary bicyclic compounds possessing various functional groups. Analysis of results obtained during this study implies that these peroxide bicyclic species along with a series of furanones and organic acids contribute to SOA growth. The effect of varying the VOC/NO<sub>x</sub> ratio on SOA formation was explored, as was the effect of acid seeding. It was found that low NO<sub>x</sub> conditions favour more rapid aerosol formation and a higher aerosol yield, a finding that points towards a role for organic peroxides in the nucleation process and SOA growth.

## 1 Introduction

Secondary organic aerosol (SOA) is formed in the atmosphere from the oxidation products of certain biogenic and anthropogenic volatile organic compounds (VOCs) (Finlayson-Pitts and Pitts Jr., 2000). One important class of such compounds known to be precursors to SOA are aromatic hydrocarbons (Stern et al., 1987; Odum et al., 1997). Possessing complex and extensive atmospheric reaction pathways, aromatic VOCs (AVOCs) have the ability to yield a wide array of secondary oxygenated and nitrated volatile, semi-volatile and non-volatile organic products which contain a multitude of different functional groups (e.g. Atkinson, 2000; Hamilton et al., 2003; Johnson et al., 2005; Sax et al., 2005; Bloss et al., 2005b).

ACPD

8, 11685–11754, 2008

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Released principally from automobile exhaust emissions, industrial scale combustion and the evaporation of fuels and solvents (Friedrich and Obermeier, 1999), AVOCs make up as much as 40% of the total mass of anthropogenic hydrocarbon emissions in the city environment (Smith et al., 1999). On the global scale total aromatic emissions are of the order  $15.8 \text{ Tg y}^{-1}$  (Tsigaridis and Kanakidou, 2003), which account for ~15% of the annual anthropogenic non-methane hydrocarbon (NMHC) budget (Bloss et al., 2005a). As well as constituting precursors to SOA production, AVOCs generally have high photochemical ozone creation potentials and hence contribute significantly towards tropospheric ozone pollution (Calvert et al., 2002; Derwent et al., 2003; Derwent et al., 2007a; Derwent et al., 2007b).

It has been established that SOA mass constitutes a major fraction of the total atmospheric loading of organic aerosol and indeed the more general class of atmospheric particulate matter, on both the local (Baltensperger et al., 2005) and the global (Kanakidou et al., 2005) scale. Under certain scenarios atmospheric SOA can comprise as much as 90% of organic aerosol mass (Kalberer et al., 2004) and 50% of the total mass of atmospheric aerosol (Kleindienst et al., 1999).

The existence of SOA in the atmosphere (and particulate matter in general) has an array of well documented consequences (e.g. Czoschke et al., 2003; Kanakidou et al., 2005; IPCC, 2007 and references therein). In brief, such negative effects range from visibility impairment on the local scale to climate change, with SOA being capable of perturbing the Earth's radiative budget via both direct and indirect mechanisms. Additionally, fine airborne particles have been shown to exert numerous detrimental effects on human health, particularly in vulnerable members of the population (Grosjean, 1992).

As highlighted in recent reviews (e.g. Seinfeld and Pankow, 2003; Kanakidou et al., 2005; Holmes, 2007), despite its crucial role in the Earth-atmosphere system, there currently remains a certain lack of understanding regarding the physical and chemical properties of SOA, its chemical composition and crucially the atmospheric processes by which it is formed.

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Over the last decade much research and many state-of-the-art techniques have been applied to the critical problem of determining SOA chemical composition, with off-line GC-MS analysis of filter samples often providing the foundation. However, such studies have supplied limited molecular level classification, with generally no more than 30% of the total SOA mass being identified (e.g. Forstner et al., 1997; Kleindienst et al., 1999; Cocker III et al., 2001; Hamilton et al., 2003; Edney et al., 2005; Surratt et al., 2006).

A series of recent discoveries have allowed significant advancement in our understanding of SOA composition and the role of low molecular mass species in aerosol growth. It has been proposed that between 20 and 50% of SOA mass could be comprised of large multi-functional macromolecular compounds known as “humic-like substances” (HULIS) (Havers et al., 1998), which would go undetected using standard GC-MS techniques. Research has suggested that such compounds are secondary in nature, being formed by heterogeneous polymerisation/oligomerisation reactions in the aerosol. For example, Jang and Kamens (Jang and Kamens, 2001) witnessed an increase in SOA yield when various gas phase aldehydic species were injected into a synthetic air matrix impregnated with acidic seed particles. The authors attribute the increase in SOA mass to heterogeneous hydration and polymerisation reactions of low molecular mass aldehydes following their transfer from the gas phase. Their findings also indicated that hemiacetal/acetal formation is also an important contributing pathway to increased SOA yields when alcohols were also present.

Numerous investigations have since confirmed the existence of polymeric/oligomeric compounds in various SOA systems of both anthropogenic (Gross et al., 2006) and biogenic (Surratt et al., 2006) origin, both in simulation chamber studies (Baltensperger et al., 2005) and in the “real” atmosphere (Kalberer et al., 2006), with molecular masses as large as 1600 Da (Gao et al., 2004). One such study by Kalberer et al. demonstrated that as much as 50% of the SOA mass formed during the photooxidation of 1,3,5-trimethylbenzene was composed of polymers (Kalberer et al., 2004). The authors proposed that the polymers, which were detected with masses as high as 1000 Da, were formed primarily through acetal polymerisation involving the known trimethylbenzene

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



photooxidation product methyl glyoxal in the presence of water.

With a large portion of current research into SOA formation geared towards investigation of the aerosol phase, there exists a distinct lack of detailed understanding of the concomitant gas phase organic components of the system. Limited work has also been conducted in elucidating the actual mechanisms of SOA formation. Recently, research has shown that the SOA forming capacity of aromatic systems is strongly related to  $[\text{NO}_x]$ , with greater SOA yields obtained under low  $\text{NO}_x$  conditions (Izumi et al., 1988; Stroud et al., 2004; Song et al., 2005; Ng et al., 2007). Conclusions from such work have inferred an important role for gas phase organic peroxides in initiating the formation of SOA (Johnson et al., 2004), but no direct evidence is available to support this.

In the present study we begin to address these issues by presenting findings from a series of comprehensive photooxidation experiments in an atmospheric simulation chamber. The main aim of the study was to monitor, in detail and with good temporal resolution, the complex array of organic gas phase oxidation products derived from a known SOA precursor and to identify potential species contributing to incipient aerosol formation and growth. In this instance the common, but less well studied anthropogenic AVOC, 1,3,5-trimethylbenzene (TMB), was chosen as a model anthropogenic SOA precursor. The effect of variation of the initial VOC/ $\text{NO}_x$  ratio on SOA formation was also explored, as was the role of potential acid-catalysed heterogeneous chemistry. As well as presenting information that provides new insight into the mechanisms of SOA forming intermediates and potential SOA forming species, this work presents the first measurements of a set of previously undetected high mass oxygen-bridged bicyclic compounds, which are formed during aromatic oxidation.

In a companion article<sup>1</sup> (here after referred to as Rickard et al., 2008) the gas phase measurements presented here are compared with the output of a box model employing

<sup>1</sup>Rickard, A. R., Wyche, K. P., Metzger, A., Monks, P. S., Ellis A. M., and Pilling, M. J.: Model-measurement comparisons of the evolution of the gas-phase precursors to secondary organic aerosol formed in the photooxidation of 1,3,5-trimethylbenzene, in preparation, 2008.

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



data extracted from the Master Chemical Mechanism (MCMv3.1; <http://mcm.leeds.ac.uk/MCM>). The findings of this complementary study support the results obtained here and in combination they provide further insight into the identity of potential SOA forming species.

## 2 Experimental

### 2.1 The Paul Scherrer Institut aerosol chamber

Experiments were carried out at the aerosol chamber facility at the Paul Scherrer Institut. The chamber comprises a single-lined collapsible bag constructed from DuPont Teflon fluorocarbon film, with a wall thickness of  $125\text{ }\mu\text{m}$  and a volume of  $27\text{ m}^3$  ( $3\times 3\times 3\text{ m}^3$ ). The chamber surface area to volume ratio ( $2\text{ m}^{-1}$ ) is relatively small when compared to most environment chambers, allowing wall effects to be minimized. The chamber bag is held by a large metal frame inside a temperature-controlled wooden housing, which was maintained at  $20^\circ\text{C}$  ( $\pm 1^\circ\text{C}$ ) during all experiments. Four 4 kW xenon arc lamps, deployed at various points inside the housing, are employed to simulate the solar spectrum (Paulsen et al., 2005).

The chamber sample gas comprised purified ambient air, which was produced by a clean air generator (AADCO Instruments Inc., USA). Chamber humidification was facilitated by bubbling the bulk matrix gas through a heated glass vessel containing high purity deionized water ( $15\text{ M}\Omega$ ) prior to the injection of other compounds. The chamber humidity was typically near 50% during each experiment.

Delivery of the VOC SOA precursor to the chamber took place via syringe injection of the liquid compound into a heated injector port, which facilitated compound volatilisation before entry into the bag. A period of 30 min was allowed for mixing to create a homogeneous sample matrix before any measurements were made.

In order to remove any potential organic impurities from the chamber and hence to eliminate unwanted artefacts from the data (in the form of SOA formed from species

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



other than the TMB), the chamber bag was scrubbed with ozone (2–7 ppmV) for 5 h, before being flushed thoroughly with purified ambient air for approximately 30 hours prior to each experiment.

On-line measurements of chamber nitric oxide (NO) and NO<sub>x</sub> concentrations were made throughout each experiment using a Monitor Labs 9841A NO<sub>x</sub> analyser (for NO<sub>x</sub> concentrations: 50–2000 ppbV) and a Thermo Environmental Instruments 42C trace level NO<sub>x</sub> photolytic converter (for NO<sub>x</sub> concentrations: 0–200 ppbV). Ozone measurements were also conducted in real-time using an ozone analyser (EnviroNics model S300). The aerosol phase was monitored using two TSI (3025 and 3022A) condensation particle counters (CPC, size range: particle diameter ( $D_p$ )  $\geq 3$  nm) and a Sampling Mobility Particle Sizer (SMPS, size range:  $15 \leq D_p \leq 690$  nm), providing information on the total number density of particles in the chamber along with particle geometric mean diameter and aerosol volume concentration (see Dommen et al., 2006 for further instrument details).

## 2.2 Experiment design

In order to explore the effect of NO<sub>x</sub> on the TMB-SOA system, experiments were conducted with various initial VOC/NO<sub>x</sub> ratios. For the first part of the study, chamber experiments were conducted with high concentrations of VOC (>500 ppbV) and NO<sub>x</sub> (>250 ppbV). For these high NO<sub>x</sub> experiments nitric oxide and nitrogen dioxide (NO<sub>2</sub>) gases (Air Liquide, Ch., grade N6.0) were added to the chamber via an inlet injection system prior to introduction of the VOC. Experiments with initial VOC/NO<sub>x</sub> ratios of approximately 2:1, 2:1 (with NO only) and 1:2 were carried out during the high NO<sub>x</sub> part of the study.

As well as conducting “high” concentration chamber experiments with input of all gases before initiation of the photochemistry, two “low” concentration experiments were conducted in order to simulate more realistic atmospheric conditions. In these experiments a constant low level source of nitrous acid (HONO) was used to supply NO to the system in place of NO and NO<sub>2</sub> gases. HONO was produced by reaction of a

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





sodium nitrite solution with sulfuric acid in a flow system. A nitrogen carrier gas was passed through the mixture continuously in order to purge nitrous acid vapour out and into the chamber bag (Taira and Yukio, 1990). This process provided a constant HONO mixing ratio of roughly 10 ppbV throughout the experiment. Consequently, the low concentration experiments had high initial VOC/NO<sub>x</sub> ratios of ~16:1. In order to provide a brief exploration into the effect of an inorganic seed, for Experiment 7, 400 pptV sulphur dioxide (SO<sub>2</sub>) gas was added to the chamber. Table 1 lists the specific starting conditions used for each experiment.

## 2.3 VOC/OVOC measurement with chemical ionisation reaction time-of-flight mass spectrometry

The gas phase organic compounds within the chamber were monitored using a newly developed chemical ionisation reaction time-of-flight mass spectrometer (CIR-TOF-MS). TOF-MS comes into its own when dealing with such complex mixtures since the entire spectrum is captured in any one instant. Furthermore, the technique is not constrained by upper mass limits and its standard resolution is usually far higher than more conventional quadrupole mass spectrometers. Therefore, important advantages of CIR-TOF-MS in this instance include the ability to detect a comprehensive set of organic compounds, including oxygenated VOCs (OVOCs) and species of quite high molecular masses and the ability to assist compound identification on the basis of accurate mass measurements. Details regarding the instrument and its performance have been given previously (Blake et al., 2003; Wyche et al., 2007), and hence only a brief and experiment-specific review is provided here.

The CIR-TOF-MS comprises a radioactive ion source/drift cell assembly, coupled to an orthogonal time-of-flight mass spectrometer equipped with a wide bore reflectron array. In the current study proton transfer was used as the means of ionization and the proton donor was the hydronium ion (H<sub>3</sub>O<sup>+</sup>) (Lindinger et al., 1993). In order to generate the primary reagent ions, water vapour was delivered to the ion source by bubbling a high purity nitrogen carrier gas (Air Liquid, Ch, grade 7.0) through a

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



glass vessel containing ultra-pure deionized water (15 M $\Omega$ ) at a rate of 30–52 sccm. Sample air from the PSI aerosol chamber was delivered to the CIR-TOF-MS at a rate of 200–275 sccm via an insulated 2 m long Teflon line and a PTFE critical orifice. Both the sample line and critical orifice were heated to 40°C ( $\pm 1^\circ\text{C}$ ) in order to limit wall losses. For brief intervals during certain experiments a particle filter was placed in the sample line to verify that all measured signals were due to gas phase species. The combined reagent and sample gas flows led to drift cell operating pressures in the range 6–9 mbar. A positive potential difference was applied across the drift cell to guide the ions into the mass spectrometer. The drift cell electric field (and therefore internal energy) was varied for certain experiments in order to enhance sensitivity to certain VOCs. The potential difference between the final two electrodes of the cell was varied to facilitate collision-induced dissociation of the ionised sample and hence to allow controlled removal of unwanted water cluster ions, i.e.  $\text{MH}^+(\text{H}_2\text{O})_n$  (where M represents the target VOC). The experiment specific drift cell  $E/N$  ratios (where  $E$  is the electric field and  $N$  is the gas number density) are provided in Table 1.

As stated earlier, an important feature of time-of-flight mass spectrometry is the ability to achieve a much higher mass resolution than alternative techniques, noticeably quadrupole mass spectrometry. The mass resolution attained in the current study was in the region of 0.01 Da and this has proved useful in confirming the assignment of several high mass peaks.

The sum of hydro and organic peroxy radicals (i.e.  $\sum(\text{HO}_2 + \sum_i \text{R}_i\text{O}_2)$ ) present in the chamber was also measured during low  $\text{NO}_x$  experiments using a dual channel Peroxy Radical Chemical Amplifier (PERCA). The PERCA deployed during this work was similar to that described in Green et al., 2006, but with inlet systems as per Monks et al., 1998.

## 2.4 Calibration issues

A wide array of compounds was detected using the CIR-TOF-MS and it was therefore impractical to carry out independent calibrations for all measured species. Conse-

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



quently, where no calibration standard was available for a given compound the calibration factor determined for a structurally similar surrogate was utilised. If no appropriate surrogate could be found, measurements are reported in terms of instrument signal (i.e. normalised ion counts per second (ncps) see Sect. 3.7). VOC yields quoted in the following discussion therefore act only as a guide for those compounds where surrogates have been employed. Table A1 in the supporting information provides comprehensive details of all VOC calibrations employed in the current study. Considering all instrument and calibration associated uncertainties (Wyche et al., 2007), the overall CIR-TOF-MS measurement errors lay within the range 2.9–27.6% (see Table A1).

Owing to experimental time constraints, a PERCA chain length calibration was not carried out following all experiments. Consequently, a typical chain length of 109 (obtained from previous experiments; Parker, 2007) was assumed to provide reasonable estimates of the peroxy radical concentrations. The amplification chain length of the PERCA varies between ~80 and 150. When combined with instrument uncertainties this gives an estimated peroxy radical uncertainty of 42% (Fleming et al., 2006a; Fleming et al., 2006b).

### 3 Results and discussion

The chamber conditions in this work can be broadly divided into two groups, high  $\text{NO}_x$  and low  $\text{NO}_x$ . In the high  $\text{NO}_x$  experiments the initial  $\text{NO}_x$  concentration was >250 ppbV, whereas low  $\text{NO}_x$  conditions corresponded to  $\text{NO}_x$  at  $\leq 5$  ppbV. The results from the high and low  $\text{NO}_x$  experiments are reported separately in the following sections. Comparisons of gas and aerosol phase measurements carried out under different VOC/ $\text{NO}_x$  regimes are utilised during the present study to help elucidate the underlying SOA formation mechanisms.

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



### 3.1 Chamber inorganic species and the SOA precursor under high NO<sub>x</sub> conditions

The majority of experiments (Experiments 1–4 and 6; see Table 1) were carried out under high NO<sub>x</sub> conditions. During these experiments the initial VOC/NO<sub>x</sub> ratio was varied between 0.54 and 2.25.

Figure 1a–d displays the temporal evolution of the major inorganic gas phase components of the chamber system and the 1,3,5-trimethylbenzene precursor in several different experiments. In all instances the experiment start time is taken from the point at which chamber lights were switched on and hence the photochemistry initiated. On average the duration of each experiment was of the order of 9–10 h.

Figure 1a summarises the findings for Experiment 6. Experiment 6 constitutes a typical example of a high NO<sub>x</sub> Experiment with VOC/NO<sub>x</sub>~2:1; hence it is used as focus for discussion. The Experiment essentially begins with the production of ground state atomic oxygen, which originates from the photolysis of NO<sub>2</sub>. This results in the subsequent production of ozone, photolysis of which in the presence of water, yields OH. OH can also be generated in such systems from HONO photolysis, which is generally produced in all chamber systems following wall reactions involving NO<sub>2</sub> (e.g. Metzger et al., 2008a<sup>2</sup>). Following its generation, OH reacts with TMB to subsequently generate a complex array of oxidation products, including organic peroxy radicals (RO<sub>2</sub>), hydroperoxy radicals (HO<sub>2</sub>) and oxygenated and nitrated VOCs (Calvert et al., 2002).

The oxidation profiles for TMB during all high NO<sub>x</sub> experiments exhibited similar behaviour, with a short initial concentration plateau corresponding to the time required to initiate the OH chemistry, followed by a peak in oxidation rate ~160 min after lights on. After this period, the TMB concentration profile was characterised by a roughly constant decay. For each high NO<sub>x</sub> experiment a plot of ln[TMB] vs. time is approx-

<sup>2</sup>Metzger, A., Dommen, J., Gaeggeler, K., Duplissy, J., Prevot, A. S. H., Kleffmann, J., Elshorbany, Y., Wisthaler, A., and Baltensperger, U.: Evaluation of 1,3,5-trimethylbenzene degradation in the detailed tropospheric chemistry mechanism MCMv3.1 using environmental chamber data, in preparation, 2008a.

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



imately linear, with no distinct change in rate with accumulation of ozone. Consequently with NO<sub>3</sub> oxidation of TMB negligible under the experimental chamber conditions used, the major chemical loss of TMB results solely from its reaction with OH. An estimation of [OH] can therefore be inferred from the TMB decay recorded by CIR-TOF-MS. For experiments with an initial VOC/NO<sub>x</sub> ratio of ~2:1, peak OH concentrations were ~0.04 pptV and experiment average concentrations were ~0.03 pptV (using  $k_{\text{OH}+1,3,5\text{TMB}} = (5.67 \pm 1.13) \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$  at  $T = 298 \text{ K}$  Calvert et al., 2002).

With the production of both HO<sub>2</sub> and RO<sub>2</sub> radicals, NO became oxidised to NO<sub>2</sub>, leading to the concentration peak seen in Fig. 1a–c. Due to the presence of the VOC (and hence RO<sub>2</sub>), the NO/NO<sub>2</sub> partitioning was such that there was a positive deviation from the photostationary state resulting in net initial ozone production (Monks, 2005). As noted in other chamber studies (e.g. Bloss et al., 2005a; Dommen et al., 2006), the peak in [NO<sub>2</sub>] and the initial accumulation of O<sub>3</sub> roughly coincide with the observed maximum rate of loss of the VOC and the peak in [OH]. Eventually, NO<sub>2</sub> is removed from the gas phase through the production of nitric acid (HNO<sub>3</sub>) via reactions on the chamber walls and incorporation into organic nitrates and the aerosol phase (Monks, 2005). As NO<sub>2</sub> chemistry constitutes the sole route to O<sub>3</sub> formation within the chamber, the removal of NO<sub>x</sub> from the system was followed by a fall in the concentration of O<sub>3</sub>. At the conclusion of Experiment 6, ~70% of the VOC precursor had been consumed and the concentrations of NO and NO<sub>2</sub> had fallen to negligible levels (Fig. 1a). For Experiment 2 (VOC/NO<sub>x</sub>~2:1) shown in Fig. 1b, initial NO<sub>x</sub> was introduced solely in the form of NO and starting concentrations were set to two times those of other high NO<sub>x</sub> experiments with VOC/NO<sub>x</sub>~2:1. To initiate the oxidation process in this instance, HONO and NO<sub>2</sub> had first to be liberated from the illuminated chamber walls following known heterogeneous chemical mechanisms (Stroud et al., 2004; Metzger et al., 2008a<sup>2</sup>).

Experiment 3 involved a reversal of the VOC/NO<sub>x</sub> ratio to a value of roughly 1:2, but still with high starting concentrations. As can be seen in Fig. 1c the NO<sub>x</sub>, O<sub>3</sub> and TMB components of the system exhibited similar profiles to those observed during the other high NO<sub>x</sub> experiments, but with a number of key exceptions. When the VOC/NO<sub>x</sub> ratio

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



was decreased to  $\sim 0.5$ , the rate of decay of TMB appeared enhanced, suggesting higher levels of oxidant. In this instance inferred OH radical levels were on average  $\sim 0.06$  pptV, i.e. twice as high as levels observed in the other high  $\text{NO}_x$  experiments. This is likely to result from balancing of the OH/ $\text{HO}_2$  ratio in the hydroxyl radical cycle, where a relatively higher proportion of NO (with respect to that of the VOC) will force a shift towards OH in the chamber  $\text{HO}_x$  balance. The impact of an elevated OH density is reflected in the amount of VOC consumed by the conclusion of the experiment, i.e. after 600 min less than 10% of the initial TMB remained. In addition to this, a lower  $\text{RO}_2/\text{NO}_x$  ratio will slow the cycling of NO to  $\text{NO}_2$  and hence delay subsequent  $\text{O}_3$  production. This effect is observed in the data, where a significant delay was indeed observed in the times at which  $\text{NO}_2$  and  $\text{O}_3$  reached their respective peaks, and at which NO reached negligible concentrations when compared to experiments with  $\text{VOC}/\text{NO}_x \sim 2:1$ .

### 3.2 Chamber inorganic species and the SOA precursor under low $\text{NO}_x$ conditions

The second component of the chamber study comprised two low  $\text{NO}_x$  experiments, Experiments 5 and 7, during which  $[\text{NO}_x]$  was kept below  $\sim 5$  ppbV. In the case of Experiment 7,  $\text{SO}_2$  gas was added to the chamber in order to generate sulphuric acid ( $\text{H}_2\text{SO}_4$ ) seed particles.

As discussed in Sect. 2.2, during the low  $\text{NO}_x$  experiments the chamber was supplied with a continuous source of NO (from HONO) at a rate greater than the sum of its removal pathways. Consequently, the chamber remained in a state of net ozone production throughout the experiment and therefore no distinct peak and fall is observed in the ozone concentration profile.

In addition to supplying the chamber with NO, HONO photolysis constituted an additional source of OH. The photolysis rate of nitrous acid ( $j(\text{HONO})$ ) for the PSI chamber has been measured as  $2.7 \times 10^{-4} \text{ s}^{-1}$ , which yields an OH production rate ( $P(\text{OH})$ ) of  $2.7 \text{ pptV s}^{-1}$  for a constant HONO value of 10 ppbV. As  $P(\text{OH})$  from the photolysis of HONO was several times larger than  $P(\text{OH})$  from ozone at any instant during the low  $\text{NO}_x$  experiments, the level of OH in the chamber was roughly constant. Evidence

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



for this can be seen in Fig. 1d, where the rate of decay of TMB during Experiment 7 remained roughly constant during the majority of the experiment. Using the rate of oxidation of TMB (as described in Sect. 3.1), the average OH concentrations in the chamber for the two low NO<sub>x</sub> experiments 5 and 7 were estimated to be ~0.05 and 0.06 pptV. Tables 1, 2 and 3 lists key measured parameters describing the evolution of the inorganic species for each experiment.

### 3.3 Chamber aerosol formation under high NO<sub>x</sub> conditions

Figure 2a–d summarise the key aerosol phase parameters for the four variants of the TMB photooxidation study, i.e. the total aerosol number density, total aerosol volume and mean geometric particle diameter.

For Experiments 1–6 no seeding was employed in the simulation chamber and hence new aerosol formation occurred via homogeneous nucleation involving certain key semi-and non-volatile oxidation products of the precursor VOC (Seinfeld and Pankow, 2003; Holmes, 2007). The nucleation event observed during Experiment 6 (high NO<sub>x</sub> experiment, VOC/NO<sub>x</sub>~2:1) is clearly evident in Fig. 2a, and is seen as a dramatic increase in the total number density of particles in the chamber at ~185 min. In this study we define nucleation to have occurred once the differential of the particle number density (with respect to time) exceeds a value of one for 3 consecutive measurements (i.e. when the particle count tends away from the baseline). Nucleation times are given for the CPC and the SMPS instruments in Table 1. However as the CPC measures particles closer in size to the nucleating cluster (i.e. ~1.5 nm), those values are employed during the following analysis and discussion.

In Experiment 6 new SOA formation continued for some 100 min, by which time a maximum number density of ~490 particles cm<sup>-3</sup> was reached (in the size range 15–690 nm). During this time, via condensation and then coagulation mechanisms, the particles grew in size to a maximum mean diameter of ~480 nm at ~490 min. The total volume of chamber SOA followed a similar trend to that of particle diameter. Ultimately the number density of SOA particles and the total suspended chamber mass

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





decreased owing to coagulation and deposition to the chamber walls. Table 2 highlights the reproducibility of aerosol phase parameters between repeat studies of the three high  $\text{NO}_x$  experiments carried out at  $\text{VOC}/\text{NO}_x \sim 2:1$  (Experiments 1, 4 and 6).

Following the analysis performed in Baltensperger et al., 2005, total SOA mass has been determined from the measured SOA volume by assuming a density of  $1.4 \text{ g cm}^{-3}$ . In the case of Experiment 6, a maximum SOA mass of  $31 \mu\text{g m}^{-3}$  was reached. As no wall loss corrections have been applied to the aerosol phase data, this value constitutes a lower limit and should be treated with care. Consequently, a “relative” SOA yield ( $Y$ ) was calculated according to Eq. 1 (after Odum et al., 1996):

$$Y = (M_0 / \Delta\text{VOC}) \times 100 \quad (1)$$

In the above expression  $M_0$  corresponds to the peak mass of SOA produced and  $\Delta\text{VOC}$  is the amount of the precursor VOC consumed at the peak SOA mass (both expressed in units of  $\mu\text{g m}^{-3}$ ). Yields for the three repeat experiments with a  $\text{VOC}/\text{NO}_x$  ratio  $\sim 2:1$  (i.e. Experiments 1, 4 and 6) were 1.9, 2.3 and 1.8%, respectively.

The temporal behaviour of the measured aerosol parameters for Experiment 2 ( $\text{VOC}/\text{NO}_x \sim 2:1$ , NO only) was similar to those of Experiments 1, 4 and 6. However, as the initial concentration of both TMB and NO was set to twice that of the other high  $\text{NO}_x$  ( $\text{VOC}/\text{NO}_x \sim 2:1$ ) experiments, an approximate two-fold increase in the maximum number density of particles was observed ( $\sim 1200 \text{ particles cm}^{-3}$ ). Also, particles grew to possess larger maximum mean diameters ( $\sim 660 \text{ nm}$ ) and the ultimate experiment SOA yield was roughly four times greater than that of the other high  $\text{NO}_x$  experiments (1, 4 and 6), at 7.5%. The findings described here for an enhanced level of starting material are consistent with those previously reported (e.g. Paulsen et al., 2005; Song et al., 2005; Gross et al., 2006).

When the starting  $\text{VOC}/\text{NO}_x$  ratio was reversed to  $\sim 1:2$  for Experiment 3, SOA formation was significantly delayed, with nucleation occurring around 215 min later than in Experiment 6. By the conclusion of Experiment 3 ( $\sim 600 \text{ min}$ ) the chamber aerosol appeared to still be in a state of growth and no distinct peak in either size or mass had

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

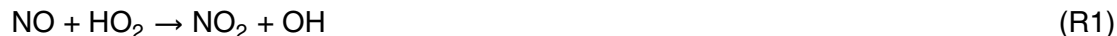
[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)



been reached. Consequently, the SOA yield was determined from the aerosol mass produced at the conclusion of the experiment. With a VOC/NO<sub>x</sub> ratio of ~1:2, a SOA yield of 0.3% was achieved, i.e. roughly an order of magnitude lower than for the larger VOC/NO<sub>x</sub> ratios. With more than 90% of the precursor VOC consumed by termination of the experiment and with primary and secondary oxidation products having reached their concentration peaks, it may be assumed that further aerosol growth after this point would be minimal.

From the above discussion and from inspection of Table 2 it is clear that for each experiment conducted under high NO<sub>x</sub> conditions a significant delay or “incubation” period was witnessed before the nucleation event. For Experiments 1, 2, 4 and 6 (VOC/NO<sub>x</sub>~2:1) this period lasted for approximately 110, 145, 190 and 185 min, respectively, and for Experiment 3 (VOC/NO<sub>x</sub>~1:2) was over twice as long at 400 min. Evidence for this incubation period has been reported for several other aromatic oxidation systems, including benzene, toluene, *o*-xylene and *m*-xylene in a number of different simulation chambers (Izumi et al., 1988; Johnson et al., 2004; Johnson et al., 2005; Song et al., 2005; Ng et al., 2007).

It has been proposed that the existence and duration of the incubation period is directly related to the presence of NO in the gas phase (Johnson et al., 2004; Johnson et al., 2005). Results obtained by Johnson et al. (2005) from a gas phase oxidation model coupled to an absorptive aerosol transfer scheme showed that the less volatile hydroperoxides, formed from the self-reactions of hydro and organic peroxy radical species (R3 and R4), were significant contributors to SOA mass. Consequently, new particle formation and growth could be closely linked to the ambient levels of NO, which may preferentially react with HO<sub>2</sub> and RO<sub>2</sub> via reactions R1 and R2 in the scheme below, limiting the capacity of the system to form peroxides:



## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

I◀

▶I

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





Johnson and co-workers (Johnson et al., 2005) proposed that once in the aerosol phase, the peroxides can take part in heterogeneous chemistry with certain aldehydic species to form peroxyhemiacetals. This thesis supports results from previous studies of various workers demonstrating the importance of heterogeneous chemistry in the aerosol, and in particular acetal and hemiacetal reactions involving carbonyl oxidation products (Jang and Kamens, 2001; Jang et al., 2003).

Through an examination of the kinetics involved with reactions R1–R4, it is possible to infer the influence of the NO concentration on gas phase hydroperoxide formation during the experiments presented here. Equation 2 below accounts for reactions R1–R4 to determine the fraction of RO<sub>2</sub> (Φ) that forms hydroperoxides:

$$\Phi = \{k_4[\text{RO}_2][\text{HO}_2]\} / \{k_4[\text{RO}_2][\text{HO}_2] + k_3[\text{RO}_2]^2 + k_2[\text{RO}_2][\text{NO}]\} \quad (2)$$

Figure 3a shows the variation of Φ with NO concentration taken from Experiment 6, for a series of HO<sub>2</sub> and RO<sub>2</sub> concentrations generated from the chamber box model employed in a companion paper (Rickard et al., 2008). Figure 3a clearly demonstrates that for the self-reaction route involving both hydro and organic peroxy radical species to become significant, either high radical levels are required (i.e. tens of pptV) or the concentration of NO must approach zero. For Φ (i.e. hence peroxide formation) to reach as much as 5% in this model, the concentration of NO must fall below 2 ppbV (with ~34 and 51 pptV HO<sub>2</sub> and RO<sub>2</sub>, respectively) and for 10%, ~1 ppbV (with ~41 and 61 pptV HO<sub>2</sub> and RO<sub>2</sub>, respectively). Comparable results have been obtained here using a chamber box model to generate radical profiles (not shown), employing a mode similar to that used by Ng et al. during chamber studies involving benzene, toluene and *m*-xylene (Ng et al., 2007).

During Experiments 1, 2, 4 and 6 (VOC/NO<sub>x</sub>~2:1), the time required for the NO concentration in the chamber to reach 2 ppbV (i.e. to approach zero) ranged from ~150 to 170 min (see Table 2). Contrasting these times with those of the nucleation event

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



in each case, we see that SOA formation occurs only as [NO] drops towards zero, adding support to the thesis that peroxide chemistry is involved in SOA formation. However, during experiments 4 and 6 there is a further time delay (of ~30 and 20 min, respectively) before particle formation occurs, implications of which are discussed in Sect. 3.5. The concentrations of NO at nucleation for the high NO<sub>x</sub> Experiments 1, 2, 4 and 6 were 16.2, 6.2, 1.2, and 1.4 ppbV, respectively. Particle growth during Experiment 1 was slower than other repeat experiments, an observation in line with slightly higher [NO] at the point of SOA formation.

The hypothesis suggesting that the NO concentration in the chamber must reach a minimal value before nucleation can occur is supported by results obtained from varying the VOC/NO<sub>x</sub> ratio. When the VOC/NO<sub>x</sub> ratio was changed from 2:1 to a nominal value of 1:2 (Experiment 3), a considerably longer time was required for the system chemistry to reduce [NO] to negligible levels (see Table 2). Correspondingly, a delay was observed in the timing of the nucleation event. In addition to this, nucleation did not occur until roughly a further 75 min after [NO] had reached minimal levels.

### 3.4 Chamber aerosol formation and peroxy radicals under low NO<sub>x</sub> conditions

Figure 2 and Table 2 demonstrate the clear difference between the nucleation times of the high and low NO<sub>x</sub> experiments. During the low NO<sub>x</sub> experiments a distinctly shorter incubation period was observed before the onset of aerosol formation, i.e. ~50 and 20 min for Experiments 5 and 7, respectively, compared to an average of ~155 min for the typical high NO<sub>x</sub> experiments (see Fig. 2d). During the low NO<sub>x</sub> (constant HONO) experiments the concentration of NO up to the point of nucleation was no greater than ~1 ppbV and an additional radical source was present to supply OH and (therefore HO<sub>2</sub>) to the matrix. Consequently, it is highly likely that radical-radical self-reaction routes (R3 and R4) dominated the fate of the RO<sub>2</sub> species from the start of the experiment. It should be noted that the length of the incubation period of each low NO<sub>x</sub> experiment (i.e. 5 and 7), is comparable to the length of the time delay between NO falling to negligible concentrations and nucleation during high NO<sub>x</sub> Experiments 4

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



and 6.

The SOA yields obtained during low NO<sub>x</sub> Experiments 5 and 7 were 7.9 and 6.2% respectively, i.e. roughly 3.5 and 24.3 times larger than those achieved under high NO<sub>x</sub> conditions of VOC/NO<sub>x</sub>~2:1 and 1:2, respectively. It should be noted that in the latter instance (Experiment 3, VOC/NO<sub>x</sub>~1:2), the experiment was conducted with the same initial TMB concentration as the low NO<sub>x</sub> experiments, and thus it is unlikely that enhanced yields under low NO<sub>x</sub> conditions are an artefact of initial precursor concentration (Ng et al., 2007). Ng et al. (2007) saw roughly 2.8 and 5.7 fold increases in SOA yields in the toluene and *m*-xylene systems, respectively, when moving from high to low NO<sub>x</sub> conditions, comparable to observations made here.

As discussed earlier, recent reports attribute the production of a greater aerosol yield in low NO<sub>x</sub> systems to chamber conditions favouring formation of the low volatility peroxides from reactions R3 and R4 (Stern et al., 1987; Jenkin et al., 2003; Johnson et al., 2004; Song et al., 2005; Ng et al., 2007). However, as discussed below the conditions of low NO<sub>x</sub> Experiments 5 and 7 also allow an early production of a variety of other organic oxidation products which may further contribute to the enhancement of SOA yield.

Elevated NO<sub>x</sub> concentrations, such as those employed during the high NO<sub>x</sub> experiments of this study, lead to interference problems in the inlet chain length chemistry when measuring peroxy radical species using the PERCA technique (Green et al., 2006; Parker, 2007). Consequently, peroxy radical data are presented only for experiments conducted under low NO<sub>x</sub> conditions. Figure 4 displays the temporal evolution of the sum of both hydro and organic peroxy radicals during Experiment 5, during which a rapid rise in peroxy radical concentration was observed from lights on to a concentration plateau of ~175 pptV by ~400 min. The onset of plateau behaviour in radical concentration was coincident with removal of the precursor VOC from the system, i.e. at plateau ~80% of the TMB had been consumed.

The temporal behaviour of the peroxy radicals during the low NO<sub>x</sub> experiments can be attributed to the constant input of OH and NO throughout the experiment and the

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



subsequent evolution of chamber ozone. As the precursor VOC constitutes the sole source of  $\text{RO}_2$ , its consumption as the experiment evolves accounts for the observed decrease in rate of peroxy radical production.

Using the partitioning theory outlined in Sect. 3.3 (Eq. 2) along with total peroxy radical and NO measurements, it is possible to demonstrate how peroxide production may proceed within the chamber under low  $\text{NO}_x$  conditions. Figure 3b shows the variation of  $\Phi$  with  $[\text{RO}_2]$  and  $[\text{NO}]$  using measured data (assuming a typical urban air  $[\text{HO}_2]/[\text{RO}_2]$  ratio of 2:3). With the NO concentrations no greater than 1 ppbV, formation of peroxides within the chamber becomes efficient as soon as the photochemistry is initiated and peroxy radicals are formed (see Figs. 1d and 4). Under low  $\text{NO}_x$  conditions Eq. 2 predicts that partitioning of  $\text{RO}_2$  to peroxides is as efficient as  $\sim 5\%$  after only the first 10 min of experiment, a result that contrasts strongly with findings from the high  $\text{NO}_x$  cases. Furthermore, Eq. 2 predicts that partitioning of  $\text{RO}_2$  to peroxides reached roughly 15% by the time of the nucleation event of Experiment 5. These experimental findings further strengthen theories proposing the crucial role played by organic peroxides during the SOA formation process.

### 3.5 Effect of inorganic seed

A comparison of the two low  $\text{NO}_x$  experiments (5 and 7) in Table 2 shows that particle formation occurred  $\sim 30$  min earlier when  $\text{SO}_2$  gas was included in the matrix. This result could be due to slightly higher OH levels measured during Experiment 7, but is most likely a consequence of  $\text{H}_2\text{SO}_4$  nucleation, which subsequently supplies a condensation surface for the condensable organic oxidation products (Holmes, 2007). In addition to this, seeding the chamber generated a larger number of particles than in other experiments. The peak particle number density during Experiment 7 reached roughly  $2200\text{ cm}^{-3}$ , compared to only  $410\text{ cm}^{-3}$  during Experiment 5. Due to the larger number of particles produced, the mean geometric aerosol diameter of the seeded SOA was slightly smaller than that produced by homogeneous nucleation, i.e.  $\sim 400$  compared to  $\sim 460\text{ nm}$ .

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Various chamber studies have shown that SOA yields generated from a VOC precursor can become enhanced in the presence of an acidic seed (Jang and Kamens, 2001; Czoschke et al., 2003; Jang et al., 2003; Limbeck et al., 2003; Gao et al., 2004; Surratt et al., 2007; Verheggen et al., 2007). Further inspection of Table 2 shows that despite the production of a greater number of particles, the aerosol yield obtained in the presence of H<sub>2</sub>SO<sub>4</sub> was no greater than the yield obtained during the companion low NO<sub>x</sub> homogeneous nucleation experiment. However, the SO<sub>2</sub> concentration employed during Experiment 7 was somewhat low (0.4 ppbV compared to >100 ppbV used by other workers, e.g. Edney et al., 2005; Kleindienst et al., 2006; Metzger et al., 2008b<sup>3</sup>); hence it is possible that the resultant [H<sub>2</sub>SO<sub>4</sub>] was too low to facilitate the acid seed effect. Therefore, with this in mind and with a lack of repeat seed experiments, the result of no yield enhancement for TMB-SOA in the presence of H<sub>2</sub>SO<sub>4</sub> is not conclusive, but is in line with findings presented by Ng et al. for two other aromatic systems: toluene and *m*-xylene (Ng et al., 2007). A more exhaustive study investigating the effect of acid seeding on TMB-SOA has been produced recently by Metzger et al. (Metzger et al., 2008b<sup>3</sup>).

### 3.6 Time-dependent SOA growth curves

In order to help elucidate the mechanisms underlying SOA formation in the TMB system, a series of time-dependent SOA growth curves have been generated, following methods employed by Song, Ng and co-workers (Song et al., 2005; Ng et al., 2007). The time-dependent growth curves essentially comprise a plot of SOA mass formed versus the amount of VOC reacted. Figure 5a presents the growth curve for Experiment 6, a typical example of the high NO<sub>x</sub> system (VOC/NO<sub>x</sub>~2:1). Initial inspection reveals the significant incubation period noted previously as the chamber concentra-

<sup>3</sup>Metzger, A., Verheggen, B., Duplissy, J., Gaeggeler, K., Dommen, J., Prevot, A. S. H., and Baltensperger, U.: Influence of sulfur dioxide on nucleation, growth rates and yield of secondary organic aerosol, in preparation, 2008b.

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



tion of  $\text{NO} \rightarrow 0$ . The incubation period is followed by a linear increase in SOA mass with expenditure of the TMB. The growth curve eventually reaches a plateau followed by decay due to particle deposition. Growth curves for all high  $\text{NO}_x$  experiments with  $\text{VOC}/\text{NO}_x \sim 2:1$  (not shown) exhibit similar behaviour, with all profiles displaying similar slopes and with all nucleation events occurring within a narrow band of reacted TMB. The time-dependent growth curves for the low  $\text{NO}_x$  experiments are also linear following nucleation, but (as noted earlier) are preceded by a much shorter incubation period than those of the high  $\text{NO}_x$  systems. As an example, Fig. 5b displays the growth curve for Experiment 7.

As noted in Sects. 3.3 and 3.4 a time delay was observed between  $[\text{NO}] \rightarrow 0$  and the nucleation event in high  $\text{NO}_x$  Experiments 3, 4 and 6, which was comparable in duration to the incubation period clearly evident in the growth curves of the low  $\text{NO}_x$  experiments (e.g. Fig. 5b). As shown above, the formation of peroxides in the low  $\text{NO}_x$  system is likely to be extremely efficient even very early into the experiment. Consequently, if organic peroxides are pivotal in TMB-SOA formation, the time delay observed after  $[\text{NO}]$  has reached minimal levels corresponds to the time required for the nucleating species to reach a critical gas phase concentration. It is also possible that the presence of a time delay in certain high  $\text{NO}_x$  experiments and the incubation zone in the absence of  $\text{NO}_x$ , are a consequence of the SOA forming species consisting of later stage oxidation products which form further down the oxidation chain, i.e. from further reaction of primary products (including certain peroxides, see discussion in Sect. 3.9). Growth curves displaying similar behaviour to those derived from the current study were presented by Song et al. for the *m*-xylene system (Song et al., 2005).

## 3.7 The gas phase organic compounds

### 3.7.1 The 1,3,5-trimethylbenzene atmospheric oxidation mechanism

Before reporting the observations derived from the CIR-TOF-MS measurements, we first outline the likely atmospheric oxidation processes of TMB that might lead to SOA

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





formation. Atmospheric oxidation of TMB may essentially be separated into two distinct pathways. One pathway is reaction via OH addition to the aromatic ring (pathway (*Pi*)) while the other involves hydrogen abstraction from a methyl group (pathway (*Pii*)). In general, the more substituted the aromatic ring, the more important the ring fragmentation route (Johnson et al., 2005; Bloss et al., 2005b). A simplified mechanism for the photochemical degradation of TMB, highlighting the most important atmospheric oxidation routes, is displayed in Fig. 6. This scheme has been constructed through an amalgamation of previous descriptions of the benzene and toluene oxidation systems (Yu et al., 1997; Atkinson, 2000; Bohn, 2001; Calvert et al., 2002; Johnson et al., 2004; Johnson et al., 2005), the MCMv3.1 TMB subset (extracted from the MCM website (<http://mcm.leeds.ac.uk/MCM>), Bloss et al., 2005a; Bloss et al., 2005b) and measurements made by CIR-TOF-MS during this study:

#### *(Pi) OH Addition to the aromatic ring*

The principal atmospheric oxidation route for TMB involves the addition of OH to the aromatic ring (branching ratio of 0.97 in the MCMv3.1), initially forming an OH-aromatic adduct (a trimethyl hydroxycyclohexadienyl radical; compound B in Fig. 6). In the presence of atmospheric levels of O<sub>2</sub> this radical is in equilibrium with its equivalent OH-aromatic-O<sub>2</sub> adduct (a trimethyl hydroxycyclohexadienyl peroxy radical) (C). The OH-aromatic-O<sub>2</sub> adduct (C) can either subsequently decompose to yield HO<sub>2</sub> and the ring retaining product 2,4,6-trimethylphenol (D), or most likely will undergo internal rearrangement to generate an O<sub>2</sub>-bridged trimethyl peroxide bicyclic radical (E) (branching ratio of 0.96 in MCMv3.1). The O<sub>2</sub>-bridged trimethyl peroxide bicyclic radical (E) can subsequently degrade through various stages of isomerisation, decomposition and scission to form the epoxy-oxy species (H) (branching ratio of 0.15 in MCMv3.1). The epoxy-oxy compound can decompose to give a variety of lower molar mass oxygenates (e.g. compounds I and J). In the atmosphere the bicyclic peroxide radical (E) will most likely undergo reaction with O<sub>2</sub> to form the peroxy radical equivalent (K) (branching ratio of 0.85 in MCMv3.1). The yields of initial products formed after addition of OH to

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





the aromatic ring of TMB in MCMv3.1 are 0.79, 0.14, and 0.04 for the trimethyl peroxide bicyclic peroxy radical (K), the epoxy-oxy species (H) and 2,4,6-trimethylphenol (D), respectively. Depending on the amount of  $\text{NO}_x$  present, the peroxide bicyclic peroxy radical (K) will degrade via a number of intermediary steps to produce a range of  $\text{O}_2$ -bridged oxygenated and nitrated compounds (compounds L–P). Some of the larger oxygenated and nitrated ring retaining products, including the multi-functional  $\text{O}_2$ -bridged species shown in Fig. 6, are likely to be sufficiently non-volatile to partition into the organic aerosol phase (Johnson et al., 2004; Johnson et al., 2005). Once inside the particle phase, these types of multi-functional compounds can take part in certain association reactions (Johnson et al., 2005). Further oxidation and ring opening processes (mainly through the oxy radical (N)) will yield an array of lower molecular mass carbonyl (including methyl glyoxal), unsaturated  $\gamma$ -dicarbonyl, acid and furanone species, some of which are shown in Fig. 6 (e.g. compounds Q–S). These low molecular mass ring fragmentation products have a tendency to be multi-functional and can be unsaturated, and therefore are generally more reactive than the parent TMB and can be oxidised further through reactions with OH and  $\text{O}_3$  and  $\text{NO}_3$ . A selection of likely, further reaction products are shown in Fig. 6. Some of these products, e.g. 3-methyl maleic anhydride (citraconic anhydride) (AC) and 3,5-dimethyl-5(2H)-2-furanone (S), can be highly polar and less volatile, and hence may be able to transfer into the organic aerosol phase (Kleindienst et al., 1999; Johnson et al., 2005).

#### *(Pii) Hydrogen abstraction from a pendant methyl group*

OH initiated hydrogen abstraction from a pendant methyl group constitutes the alternative oxidation route for TMB in the atmosphere, and represents the major ring retaining pathway (other than the formation of 2,4,6-trimethyl phenol as described above). Eventually, following hydrogen abstraction, reaction with  $\text{O}_2$ , and subsequent radical reactions (e.g. with NO,  $\text{RO}_2$ ,  $\text{HO}_2$  and OH), 3,5 dimethyl benzaldehyde (W) is formed with a yield of  $\sim 0.03$  according to MCMv3.1 (Bloss et al., 2005b).

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



### 3.8 Measurement of the gas phase organic compounds

Figure 7a–d displays the CIR-TOF-MS mass spectra recorded after 400 min of irradiation during Experiments 6, 3, 2 and 7, with VOC/NO<sub>x</sub> ratios of around 2:1, 1:2, 2:1 (NO only) and 17:1, respectively. All of the mass spectra have been normalised to 10<sup>6</sup> primary reagent ion counts (i.e. the sum of the H<sub>3</sub>O<sup>+</sup> and H<sub>3</sub>O<sup>+</sup>.H<sub>2</sub>O signals) and have been background subtracted. Consequently, all signals stated here are quoted in units of normalised counts per second i.e. ncps (de Gouw et al., 2003).

During a typical high NO<sub>x</sub> chamber experiment (and depending on the drift cell conditions employed) around 60 peaks were recorded in the mass spectra between  $m/z$  0 and 300, with around 30 peaks possessing a mass greater than that of the precursor VOC ( $m/z$  121). In contrast, roughly 50 significant features were recorded during the low NO<sub>x</sub> experiments, with around 20 of those possessing a mass greater than that of the precursor. It should be noted, however, that this difference could be attributed to the use of a lower precursor concentration during the low NO<sub>x</sub> studies where detection limits of the instrument become an issue (see Wyche et al., 2007 for further information regarding detection limits). The number of spectral features quoted here includes features present due to fragment ions as well as parent ions, and hence does not necessarily represent the total diversity of organic species in the chamber. For brief periods during certain experiments, the electric field applied across the collision cell in the CIR-TOF-MS drift tube was increased to produce more energetic collisions, and thus to identify and help exclude any possible molecular ion water cluster products (i.e. MH<sup>+</sup>.(H<sub>2</sub>O)<sub>*n*</sub>).

The major spectral features common to all experiments are listed in Table 4 along with, where possible, a tentative compound assignment. Table 4 also gives a chamber “appearance time” for each compound, defined as the time at which the signal for a given spectral feature exceeds the mean background signal plus three times its standard deviation. All compound assignments have been made using a combination of information, namely accurate mass measurements, appearance time, subsequent

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

I◀

▶I

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



temporal profile, and data available from the MCMv3.1 box model simulations (see Rickard et al., 2008).

### 3.8.1 Behaviour of the gas phase organics under high NO<sub>x</sub> conditions

As a focus for discussion, the evolution of the entire measured VOC system of Experiment 6 is presented in Fig. 8. General features of note include the appearance of most species within the first 50–100 min of the experiment, including many high mass oxidation products. The high NO<sub>x</sub> photooxidation system of TMB is also characterised by a peak in concentration of the heavier species around the mid-point of the experiment (~200–300 min). The lower molecular mass features demonstrate a continual rise in intensity up to the end of the experiment.

Looking more closely at the features recorded by CIR-TOF-MS (Table 4), it is possible to follow the system evolution as outlined in Fig. 6. Two of the earliest compounds to appear in the oxidation chain are the ring retaining compounds, 2,4,6-trimethylphenol (D) and 3,5-dimethylbenzaldehyde (W). Both of which were measured in the chamber as protonated parent ions, i.e.  $m/z$  137 and 135, respectively. 2,4,6-trimethylphenol and 3,5-dimethylbenzaldehyde were measured with peak concentrations of 0.6 and 7 ppbV, respectively.

As noted in Sect. 3.7.1, the majority of mass transit in the TMB oxidation system occurs via addition of OH to the aromatic ring followed by production of the trimethyl peroxide bicyclic radical (E) and its peroxy radical counterpart (K). Various subsequent pathways shown in Fig. 6 can lead to an array of O<sub>2</sub>-bridged aromatic compounds (L–P). We report here the first firm evidence for the existence of these O<sub>2</sub>-bridged species along with documentation of their real-time evolution, as measured by CIR-TOF-MS. As summarised in Table 4, peaks consistent with the O<sub>2</sub>-bridged nitrate (L), diol (O) and ketone (P) were recorded at  $m/z$  232, 169 and 185, respectively. Two fragment ions of the nitrate were also measured (at  $m/z$  214 and 109), as was a signal tentatively assigned to be the aromatic ring fragment of the O<sub>2</sub>-bridged species ( $m/z$  125). No ion corresponding to the protonated O<sub>2</sub>-bridged peroxide (M) was measured. Comparison

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



of the measured temporal profiles of the O<sub>2</sub>-bridged species with simulations using a chamber box model incorporating detailed TMB degradation chemistry taken from the MCMv3.1 is discussed in the companion modelling paper (Rickard et al., 2008).

Due to relatively high levels of NO early in the experiment, the O<sub>2</sub>-bridged nitrate (L) is the first of the triumvirate to appear in the chamber, at ~10–50 min. The O<sub>2</sub>-bridged nitrate is formed in relatively high yield when compared to the other aromatic systems (Bloss et al., 2005b). As the chamber matrix evolves and levels of HO<sub>2</sub> and RO<sub>2</sub> increase, the O<sub>2</sub>-bridged diol and ketone (and presumably the peroxide (M): see Rickard et al., 2008) are produced, appearing roughly together at ~40–60 min.

The concentration-time profiles of the measured O<sub>2</sub>-bridged bicyclic species are shown in Fig. 9a. The primary bicyclic nitrate exists in a state of production whilst NO is present in the chamber, up to a peak near 250 min, followed by decay as the precursor TMB is consumed and as chamber NO<sub>x</sub> falls towards zero. The O<sub>2</sub>-bridged diol and ketone follow a similar profile to the nitrate early in the experiment but continue on a steady rise as HO<sub>2</sub> and RO<sub>2</sub> become more prevalent within the chamber.

According to the mechanism outlined in Fig. 6, the O<sub>2</sub>-bridged ketone (P) and alkoxy radical (N) act as conduits for further mass transit through the oxidation system. Both compounds are liable to undergo ring cleavage to yield an array of lower molecular mass oxygenated and nitrated compounds, the first and most abundant of which are methyl glyoxal (Q) and 3,5-dimethyl-5(2H)-2-furanone (S), measured as protonated parent ions at *m/z* 73 and 113, respectively. A variety of oxygenated species, all of nominal mass 112, appear in the TMB oxidation chain and were measured collectively at *m/z* 113 (i.e. protonated) by CIR-TOF-MS. Along with 3,5-dimethyl-5(2H)-2-furanone, laboratory studies have identified these to be the furanones, 3,5-dimethyl-3(2H)-2-furanone (AF) and 3-methyl-furan-2,5-dione (methyl maleic anhydride) (AC), and the -dicarbonyl 2-methyl-4-oxo-2-pentenal (R) (Smith et al., 1999). Also observed here in the chamber matrix was a fourth furanone, 3-methyl-5-methylidene-5(2H)-2-furanone, measured at *m/z* 111 (AE) (Smith et al., 1999).

Both methyl glyoxal and the *m/z* 113 compounds are amongst the first oxidation

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

products to appear in the chamber (after ~3–30 min), being formed via a series of highly reactive radical intermediates during the early, NO<sub>x</sub> dominated stages of the high NO<sub>x</sub> experiment. As shown in Fig. 9b, the concentrations of methyl glyoxal, 3-methy-5-methylidene-5(2H)-2-furanone and the *m/z* 113 species rise rapidly to peaks of ~110, 30 and 65 ppbV, at roughly 320, 450 and 170 min, respectively. Eventually the chemistry generating these oxidation products reaches steady state, as indicated by the observed concentration plateaus.

Throughout the experiment methyl glyoxal, methyl-5-methylidene-5(2H)-2-furanone and the *m/z* 113 species were amongst the most dominant features of the mass spectrum, being produced first via the alkoxy radical and the bicyclic nitrate, and subsequently through the HO<sub>2</sub> and RO<sub>2</sub> controlled pathways. At peak concentrations the (mass percent) VOC yields (*Y*<sub>VOC</sub>) for these compounds were estimated to be ~20, 8 and 40%, respectively, accounting for a significant fraction of mass within the system.

As the oxidation process progressed a multitude of organic species with a variety of functional groups were formed within the chamber, many of which were detected by CIR-TOF-MS (see Table 4). Figure 9c gives the concentration-time profiles for three such compounds formed following ring cleavage, the multifunctional tertiary products 2-methyl-4-oxo-pent-2-enoic acid and 3-acetyl-2-methyl-oxirane-2-carbaldehyde (measured together at *m/z* 129) and hydroxy acetone (*m/z* 75). Collision energy studies have shown that 2-methyl-4-oxo-pent-2-enoic acid also undergoes a small amount of dehydration following PTR to yield a fragment of *m/z* 111. Also given in Fig. 9c is the signal measured at *m/z* 43, a generic marker for carbonyls using the PTR-MS technique (Blake et al., 2006). All such later stage oxidation products displayed similar behaviour, a steady rise to plateau roughly coinciding with peak aerosol mass. Strong signals corresponding to nitrated VOCs (even *m/z* number and low mass excess) were also measured further down the oxidation chain. These included peroxy acetyl nitrate (PAN) (*m/z* 46, Hansel and Wisthaler, 2000) and two unidentified compounds of *m/z* 96 and 136. Signals corresponding to pyruvic acid (*m/z* 89) and formaldehyde (*m/z* 31), two potential monomer units for the TMB oligomer (Kalberer et al., 2004),

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

were also measured in all experiments.

Further inspection of Table 4 shows that a number of other simple organic acids were observed in the gas phase, including hydroxy acetic acid ( $m/z$  77), acetic acid ( $m/z$  61) and formic acid ( $m/z$  47). As shown in Fig. 9d and Table 4, the various late stage acids appeared in the chamber ~20–200 min after lights on. Concentrations of hydroxy acetic acid rose steadily to a peak of around 30 ppbV at 400 min ( $Y_{\text{VOC}}=6\%$ ) followed by a steady decline. Both formic and acetic acid levels continued to rise throughout Experiment 6 as the system became more oxidised, with concentrations eventually reaching 100–120 ppbV ( $Y_{\text{VOC}}\sim 11$  and 16%, respectively). It should be noted that during “blank” experiments (no precursor VOC), both formic and acetic acid were observed in the gas phase following liberation from the illuminated chamber walls. After ~7 h of blank experiment ~10 ppbV of both formic and acetic acid was measured; hence concentrations quoted here constitute an upper limit and should be considered with care. However, Fisseha and colleagues (Fisseha et al., 2004) recently recorded similar gas phase concentrations of formic acid during TMB photooxidation (~80 ppbV after 9 h), along with significant levels within the aerosol ( $\sim 15 \mu\text{g m}^{-3}$  at peak aerosol concentration). They presented lower acetic acid concentrations than were measured here (~30 ppbV), with differences most likely explained by potential contribution to mass channel 61 from other species in the CIR-TOF-MS measurements (primarily fragment ions derived from other organic acids).

### 3.8.2 Variation of the VOC/ $\text{NO}_x$ ratio under high $\text{NO}_x$ conditions

When  $\text{NO}_x$  was initially introduced only in the form of NO (Experiment 2), the distribution and variety of ions within the mass spectrum and their concentration-time profiles were generally very similar to those of other experiments with initial VOC/ $\text{NO}_x\sim 2:1$ . The main exception to this was a delay in the appearance times of most compounds, corresponding to the time required to liberate HONO from reactions on the chamber walls and hence for the radical chemistry to initiate. Also, the oxidation products reached higher peak concentrations due to the enhanced level of starting material, but ultimately

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



achieved similar yields to the other experiments of VOC/NO<sub>x</sub>~2:1 (see Table A2).

The behaviour of the VOC component of the chamber differed more significantly when the VOC/NO<sub>x</sub> ratio was reversed to a value of ~1:2. The most obvious point of note was that despite generally exhibiting similar temporal behaviour to other high NO<sub>x</sub> experiments, the oxidation products of the reverse system took significantly longer to appear and achieve peak concentrations.

### 3.8.3 Variation of the VOC/NO<sub>x</sub> ratio, low NO<sub>x</sub> conditions

Following observations of the aerosol phase, the composition and behaviour of the gas phase organics of the low NO<sub>x</sub> systems (Experiments 5 and 7, VOC/NO<sub>x</sub>~16:1) show significant differences to those of the high NO<sub>x</sub> experiments. Along with exhibiting significantly earlier nucleation events, due to the presence of the HONO radical source Experiments 5 and 7 were also characterised by the appearance of most oxidation products much sooner than in all other experiments (see Table 4). Figure 10 shows that, once present in the chamber, the TMB oxidation products exhibited significantly different temporal behaviour under low NO<sub>x</sub> conditions when compared to other experiments. The majority of primary oxidation products were observed to rise more gradually from “lights on” to a concentration plateau, rather than a distinct peak. Consequently, the point of maximum concentration often occurred later than in other experiments, e.g. methyl glyoxal (*m/z* 73) and the *m/z* 113 compounds reached maxima around 70–80 min later than in Experiment 6, achieving ~50 and 20 ppbV, respectively. Correspondingly the later stage oxidation products also presented different temporal profiles. As seen in Fig. 10c and d, the tertiary products presented more linear growth profiles early in the experiment, being produced more rapidly due to the presence of an OH source. The “start-up” lag seen in other experiments, corresponding to the time required to establish the OH cycle, is absent. During low NO<sub>x</sub> experiments, the tertiary products were often characterised by linear profiles due to a roughly constant level of oxidant.

Most VOC yields (determined for the calibrated compounds) during the low NO<sub>x</sub>

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





experiments were similar in magnitude to those of the high NO<sub>x</sub> experiments of VOC/NO<sub>x</sub>~2:1, with some significant exceptions. Hydroxy acetic acid, acetic acid and formic acid yields obtained during low NO<sub>x</sub> experiments were on average significantly larger than those of high NO<sub>x</sub> experiments, i.e. 14, 33 and 49% compared to 4, 15 and 13%, respectively. Yields for methyl glyoxal and the *m/z* 113 compounds were slightly lower under low NO<sub>x</sub> conditions, namely ~20 and 30%, respectively.

### 3.8.4 Elucidating the gas phase oxidation mechanisms

In order to evaluate the chemical mechanism underlying the TMB photooxidation system, at the conclusion of certain experiments chamber lights were switched off and the total chamber ozone was titrated from the system with the addition of excess NO to the matrix. During Experiments 6 and 7 the chamber lights were switched off at 460 and 550 min, respectively, with the addition of NO some 60 and 30 min later. The effect of this “dark phase” on the inorganic components of the matrix and the VOCs for Experiments 6 and 7 can be seen in Figs. 1a and d, 9 and 10.

During the dark phase the photochemically driven pathways become ‘switched off’ as photolysis and OH production from both ozone and HONO cease. Also, as the chamber ozone is titrated away, chemistry occurring via ozonolysis reactions becomes negligible. Consequently, the system chemistry is switched from a regime where reactions of RO<sub>2</sub> are controlled by OH and HO<sub>2</sub> to one in which the majority of RO<sub>2</sub> species are removed from the system following reaction with the injected NO. This results in a “burst” in production of NO<sub>2</sub> and to a minor extent nitrogenated and carbonyl compounds. Manipulating the chemistry in this manner and observing the resultant effect on the VOC evolution provides key insight into the chemistry involved.

The concentration-time profile of the peroxide bicyclic ketone, seen in Fig. 9a, began to fall significantly when chamber lights were switched off, suggesting that its production must result from reactions involving RO<sub>2</sub>, HO<sub>2</sub> and OH as detailed in Fig. 6. As the photolytic formation of radicals was “switched off” under dark phase conditions, production of the bicyclic ketone was no longer possible and the chamber concentration

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





began to decay due to the instability of this species. Conversely during the dark phase, the fall in concentration of the bicyclic nitrate was arrested before levelling off to plateau as its major loss process (i.e. photolysis) was switched off.

Following the addition of NO to the chamber a significant increase in the signal measured at  $m/z$  113 was observed. This response is essentially a consequence of the parent O<sub>2</sub>-bridged species decomposing through ring opening pathways to yield various (isobaric) oxygenated products. For example following the photooxidation mechanism outlined in Fig. 6, it is likely that the peroxide bicyclic ketone decays via several intermediate steps to 3,5-dimethyl-5(2H)-2-furanone, verifying this compound's significant contribution to the signal measured at  $m/z$  113. Such findings highlight the importance of reaction routes involving the bicyclic ketone and nitrate species during the early stages of the experiment in the production of other potentially crucial SOA forming oxidation products (see Sect. 3.9).

### 3.9 Principal component analysis

As noted by Baltensperger et al. (Baltensperger et al., 2005) the VOCs observed in the oxidation of TMB can be separated into several distinct categories according to their temporal profiles. In order to better identify trends within the time series data, a Principal Component Analysis (PCA, Martens and Næs) was carried out for each experiment. PCA is an exploratory data analysis technique that will summarise correlated time behaviour of certain masses into a set of principal components. Each principal component consists of a pair of vectors: the scores vector (depicting time related behaviour) and the loadings vector (representing how strongly this behaviour is represented on each of the masses). The PCA algorithm will first find the strongest collective time trend in the data and its associated mass spectrum, followed by the second strongest and so on. Consequently, it may therefore be possible to represent the whole experiment with only a few principal components. Ultimately the PCA can be used to identify which compounds are related in the oxidation system.

Generally, during each of the PC analyses the vast majority of the temporal variability

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



was captured by the first three principal components (PC1 accounted for ~75–95% of the variance, PC2 ~4–22% and PC3 only ~0.6–1.5%). As an example of the high NO<sub>x</sub> data, the scores and loading plots obtained from a PCA conducted for Experiment 6 are given in Fig. 11a. The scores plots generated for PC1 for each high NO<sub>x</sub> experiment exhibited roughly the same pattern, i.e. a sigmoidal rise to peak and plateau. The most significant masses comprising the corresponding loadings vector were *m/z* 43 (carbonyl marker), 46 (PAN marker), 61 (acetic acid), 73 (methyl glyoxal), 77 (hydroxyl acetic acid), 87 (unidentified), 111 (3-methyl-5-methylidene-5(2H)-2-furanone) and 185 (the O<sub>2</sub>-bridged ketone). All of these masses (except *m/z* 185) constitute secondary or tertiary oxidation products of the TMB system (although methyl glyoxal also constitutes a primary product). The PAN and acetic acid signals were the greatest contributors towards the first principal component in all high NO<sub>x</sub> experiments.

The scores generated for PC2 were characterised by a rapid rise to peak followed by a similarly steep decay to steady state. The most significant corresponding loadings were *m/z* 45 (methyl glyoxal fragment), 73 (methyl glyoxal), 85 (*m/z* 113 fragment), 113 (isobaric furanone and  $\delta$ -dicarbonyl ring opening products), 125 (bicyclic fragment), 135 (3,5-dimethyl benzaldehyde), 214 and 232 (bicyclic nitrate). These compounds constitute the primary oxidation products of the TMB oxidation system. The *m/z* 73 and 113 signals were the greatest contributors towards the second principal component in all high NO<sub>x</sub> experiments. PC3 accounts for very little of the variance within all experiments, only ~1% and is composed mainly of three significant loadings corresponding to masses 47, 61 and 113.

The PCA for low NO<sub>x</sub> Experiment 7 is shown in Fig. 11b. Comparison of the scores plots with those of Experiment 6 (Fig. 11a) demonstrates the dramatic differences in the temporal behavior of the oxidation products, with no evidence of an incubation period in the VOC chemistry, i.e. the primary, secondary and tertiary products of oxidation appear in the system early on in experiment. PC1 for the low NO<sub>x</sub> system is primarily composed of the same compounds as in the high NO<sub>x</sub> system with, however, a different distribution of abundances. Under low NO<sub>x</sub> conditions *m/z* 45, 46, 73, and 111 all show

**SOA Formation from  
1,3,5-TMB**

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



significantly lower contributions to the secondary products, although  $m/z$  61 remains the greatest contributor, suggesting a more dominant role for acetic acid in the absence of  $\text{NO}_x$ . In contrast to this, PC2 is composed of a slightly different set of masses with distinctly different abundances. Masses 45, 73, 97 (unidentified), 125, 135 and particularly 111 all give stronger contributions than in the high  $\text{NO}_x$  experiments. Contrary to the high  $\text{NO}_x$  system, the second principal component also contains contributions from masses 101 (unidentified), 129 (organic acid), 139 (organic peroxide), 169 ( $\text{O}_2$ -bridged diol) and 185. These findings suggest that although ultimately the same end stage oxidation products are reached, during the early stages of the low  $\text{NO}_x$  experiments (i.e. approximately around the time of nucleation) the system chemistry is somewhat different, generating an organic gas phase matrix that is more strongly dominated by the primary  $\text{O}_2$ -bridged bicyclics, methyl glyoxal and the  $m/z$  113 compounds. This finding implies therefore that such species may play some role in the formation of aromatic SOA.

### 3.10 Identification of compounds contributing to SOA formation and growth

Although a large fraction of SOA mass remains to be identified, recent studies into the composition of aerosol formed from aromatic compounds has highlighted the presence of a discrete set of organic species originating directly from gas phase oxidation of the precursor. Of these compounds previously identified within the aerosol, several were measured (or their analogous counterparts were measured) in the gas phase during the present study, including 3,5-dimethylbenzaldehyde (Hamilton et al., 2003) from the ring retaining route, certain of the isobaric  $m/z$  113 furanones (Forstner et al., 1997; Hamilton et al., 2003) and methyl glyoxal (Kalberer et al., 2004) from the ring opening route, along with the later stage decay products hydroxy acetone, glycoaldehyde (Cocker III et al., 2001), formic acid and acetic acid (Fisseha et al., 2004).

For the gas phase species to take part in the SOA formation process, first of all their presence in the chamber must coincide with or precede the onset of nucleation. By the time of nucleation in each high  $\text{NO}_x$  experiment, virtually all of the measured

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



organic species had appeared within the chamber and hence (where possible) were available for partitioning. In contrast, a more select group of only 13 spectral features were present in the mass spectra of both low NO<sub>x</sub> experiments prior to nucleation, and hence available to the aerosol. This result implies that the early stage aerosol in the low NO<sub>x</sub> systems may be less compositionally diverse.

Several of the “early” features of the low NO<sub>x</sub> system were observed within the first few minutes of experiment: these include, the O<sub>2</sub>-bridged nitrate (at *m/z* 232, 214 and 109), diol (*m/z* 169), and fragment (*m/z* 125), methyl glyoxal (*m/z* 73) and the *m/z* 113 ring opening compounds. Other notable cases of early appearance include, the O<sub>2</sub>-bridged ketone, 3,5-dimethyl benzaldehyde, hydroxy acetic acid, acetic acid and the carbonyl marker (*m/z* 185, 137, 77, 61 and 43, respectively). As some organic compounds are not easily ionised using the proton transfer reaction technique (e.g. peroxides) and as detection limits may have excluded some compounds, it is not possible at present to conclusively assign the nucleating species. However, with only the above listed compounds measured before nucleation in every experiment, it is possible that at least some of these species will be of some importance in the SOA formation process.

The appearance times of the majority of the oxidation products during low NO<sub>x</sub> Experiment 5 were slightly later than in the corresponding low NO<sub>x</sub> Experiment 7, as was the time of the nucleation event. Although nucleation during Experiment 7 was influenced by the presence of the inorganic seed particles, the slightly higher [OH] would have facilitated faster oxidation and therefore earlier SOA formation. A similar trend was also noted when the VOC/NO<sub>x</sub> ratio was set to ~1:2. Here the appearance times of most of the TMB oxidation products were significantly delayed with respect to all other experiments. For example, methyl glyoxal (*m/z* 73) and the *m/z* 113 compounds appeared ~ 30 minutes later and the signals observed in mass channels representative of the primary bicyclic compounds (e.g. *m/z* 214, 109 and 125) a full hour later than in Experiment 6 (see Table 4 for further comparison). Subsequently methyl glyoxal, the *m/z* 113 species.

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

As noted above, the low NO<sub>x</sub> system was characterised by an enhancement in the yields for certain gas phase species, including several organic acids. Hydroxy acetic acid, acetic acid and formic acid yields during the low NO<sub>x</sub> experiments were on average ~3.5, 2.2 and 3.7 times larger than during the high NO<sub>x</sub> experiments of VOC/NO<sub>x</sub>~2:1 and 1.5, 2.8 and 6.8 times larger than during the high NO<sub>x</sub> Experiment 3 of VOC/NO<sub>x</sub>~1:2. As Experiment 3 was conducted with the same initial TMB concentration as the two low NO<sub>x</sub> experiments, yield concentration artefacts suggested by some authors can be ruled out (Ng et al., 2007).

Considering that these organic acids were available in the gas phase from early on in all experiments it is possible that their enhanced gas phase yields were at least in some part responsible for the observed increase in aerosol yields obtained under low NO<sub>x</sub> conditions, thus supplying confirmation to recent reports concerning the importance of organic acids in the composition of SOA. For example, Fisseha et al. (2004) have shown that around the point of maximum aerosol number density, organic acids comprised as much as 43% of aerosol mass. As well as simply being detected in the aerosol phase, evidence has come to light implicating that such organic acids may become incorporated into polymer-like structures found within SOA (Gross et al., 2006; Kalberer et al., 2006). Other findings published recently by various authors indicate that an acidic environment is crucial for the formation of such polymer species via various mechanistic pathways (Jang and Kamens, 2001; Czoschke et al., 2003; Limbeck et al., 2003; Gao et al., 2004; Tolocka et al., 2004; Northcross and Jang, 2007; Surratt et al., 2007; Verheggen et al., 2007). However as noted above, no distinct difference in aerosol yield was obtained between the homogeneous nucleation Experiment 5 and the acid-seeded Experiment 7. It would seem reasonable to assume therefore that if enough SO<sub>2</sub> was present to cause an acid seed effect and that the observed enhancement in aerosol yield is related to the enhancement in yields of the gaseous organic acid, then the levels of acids produced under low NO<sub>x</sub> conditions were large enough to facilitate any acid-catalysed polymerisation without the need for the inorganic acid surface. Alternatively, the organic acids may contribute to SOA mass without involvement

**SOA Formation from  
1,3,5-TMB**

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

I◀

▶I

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



in additional acid-catalysed polymerisation.

With no calibration method or reliable kinetic information available for the primary bicyclic compounds, it is not possible at present to derive their absolute concentrations or yields. However, pseudo yields may be derived by applying the CIR-TOF-MS sensitivity for a structurally similar compound, and in this instance *m*-tolualdehyde was employed. Regardless of the absolute values obtained, a ratio of the yields for the low versus high NO<sub>x</sub> experiments can be used to infer the importance of the primary bicyclic species in the SOA formation process. Using data from experiments 6 and 7, the ratio of pseudo yields obtained for  $\sum(m/z\ 109+214+232)$  was 1.36, suggesting a slight enhancement in the bicyclic nitrate under low NO<sub>x</sub> conditions. The corresponding ratios for *m/z* 169 and 185 were 5.97 and 2.89, respectively, indicating much stronger production of the O<sub>2</sub>-bridged diol and ketone in the absence of NO<sub>x</sub>. Similar yield ratios were obtained for the measured O<sub>2</sub>-bridged compounds when comparing high and low NO<sub>x</sub> experiments with the same starting concentration of TMB (i.e. Experiments 3 and 7, respectively).

As with the organic acids, the increased yield of the O<sub>2</sub>-bridged compounds could explain the enhanced SOA yield observed under low NO<sub>x</sub> conditions, particularly when supported with evidence of their appearance in the chamber prior to nucleation in each experiment. Furthermore, modelling studies by Stroud et al. (Stroud et al., 2004) and Johnson et al. (Johnson et al., 2005) have shown that the analogous O<sub>2</sub>-bridged nitrate (as well as some of the other multi-functional O<sub>2</sub>-bridged products) in the toluene system and the O<sub>2</sub>-bridged ketone in the TMB system are liable to undergo partitioning to the aerosol phase and make a significant contribution to the simulated SOA mass.

Using the methodology applied by Ng et al. (Ng et al., 2006) it is possible to glean further information regarding which species contribute to SOA growth via close inspection of their time series profiles. The concentration peaks of the O<sub>2</sub>-bridged nitrate, the unidentified nitrate at *m/z* 136 and the isobaric *m/z* 113 oxygenates roughly coincide with the nucleation event: indeed it was observed that a shift in the time of peak was matched by a corresponding shift in the time of nucleation. Plotting the mass of these

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



compounds consumed (or lost) after their concentration peak versus SOA mass produced (up to the point of maximum mass) gives a strong correlation. An example of this is given in Fig. 12a and b for the nitrate of  $m/z$  136.

The correlation plots of  $O_2$ -bridged nitrate for experiments conducted under high  $NO_x$  conditions are similar to those conducted under low  $NO_x$  (plots for Experiments 6 and 7, given in Fig. 13a and b). The correlation between mass lost and SOA mass produced indicates that the  $O_2$ -bridged nitrate contributes to SOA growth, either by direct partitioning or via further reaction generating condensable products. A steeper line fit during the low  $NO_x$  experiment suggests more rapid contribution in the absence of  $NO_x$  (see Fig. 13 for line fit coefficients). The presence of a non-zero intercept on the ordinate axis ( $\sim 14\text{--}24\ \mu\text{g m}^{-3}$ ) implies that a given amount of SOA mass was formed before any contribution to SOA growth from the  $O_2$ -bridged nitrate.

Correlation plots for loss of the nitrate at  $m/z$  136 (not shown) and the  $m/z$  113 compounds under low  $NO_x$  conditions (Fig. 13d) are very similar to those of the bicyclic nitrate. Hence, similarly under low  $NO_x$  conditions it appears that the nitrate of  $m/z$  136 and one or more of the compounds measured at  $m/z$  113 contribute to SOA growth once SOA has formed. Under high  $NO_x$  the corresponding correlations are very strong (Figs. 12b and 13c), but as with the bicyclic nitrate the gradient of the line fit remains steepest under low  $NO_x$  conditions. For both  $m/z$  136 and 113 under high  $NO_x$  conditions, there exists a small non-zero intercept on the abscissa, suggesting that either no or very little SOA mass was formed prior to loss of these compounds from the gas phase. This result suggests that as well as contributing to SOA growth, the nitrate of  $m/z$  136 and the compounds of  $m/z$  113 may play some role in particle formation under high  $NO_x$  conditions.

It would seem from the evidence presented here that the  $O_2$ -bridged nitrate and  $m/z$  113 compounds contribute towards SOA growth, along with compounds such as the unidentified nitrate ( $m/z$  136), the  $O_2$ -bridged diol and the lower molecular mass organic acids. However, evidence obtained from the low  $NO_x$  experiments suggests that the presence of other species is required to initiate nucleation. From the discussion

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





presented here two likely candidates for the role of “nucleating species” are:

1. O<sub>2</sub>-bridged ketone. The bicyclic ketone is present in the gas phase before nucleation in all experiments and has a temporal profile that grows in line with SOA mass. Furthermore, the higher gas phase yield for the bicyclic ketone under low NO<sub>x</sub> conditions is matched by an ultimately higher aerosol yield. This suggestion also supports modelling studies of Johnson et al., who propose significant partitioning of the O<sub>2</sub>-bridged ketone to the aerosol phase in their gas-aerosol coupled box model (Johnson et al., 2005).
2. O<sub>2</sub>-bridged peroxide. As discussed in Sects. 3.3–3.5 there exists evidence from this work and from that of previous studies, that organic peroxides may play a significant role in SOA formation and growth. Considering the mechanism outlined in Fig. 6, the most dominant organic peroxide available in the early chamber matrix is the O<sub>2</sub>-bridged peroxide (compound M), formed from the parent O<sub>2</sub>-bridged peroxy radical (K) reacting with HO<sub>2</sub>. No direct measurements of the bicyclic peroxide were made within this study; however from observations of the peroxy radical behaviour and from the partitioning theory of equation E2 (see Fig. 3), it is highly likely that the O<sub>2</sub>-bridged peroxide would have been present in the chamber prior to nucleation in each experiment. We discuss the potential role of the O<sub>2</sub>-bridged peroxide in SOA formation and growth in more detail in a companion modelling paper, utilising comparison between the measurements described here and modelling results obtained from a chamber box model (Rickard et al., 2008).

## 4 Conclusions

The work presented here constitutes the most comprehensive set of gas phase measurements made to date describing the unexplored composition and evolution of the organic oxidation products of an anthropogenic SOA precursor. VOC measurements

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





made by CIR-TOF-MS include gas phase oxidation products with the highest mass observed in aerosol simulation experiments so far. Furthermore, the high mass resolution available in TOF-MS has helped us to identify certain primary bicyclic oxidation products, measurements of which have not previously been reported in the literature, which

5 crucially give support to our current understanding of aromatic hydrocarbon oxidation. Moreover, compound appearance times, temporal behaviour and enhanced yields under low NO<sub>x</sub> conditions (that correlate with enhanced SOA yields), imply a role for the oxygen-bridged species and certain organic acids in the growth of TMB-SOA.

Variation of the initial chamber NO<sub>x</sub> conditions and time-dependent SOA growth

10 curves indicate a potential role for various other (multi-functional) gas phase organics in SOA growth, which appear at various stages in the oxidation chain. These include, 3,5-dimethylbenzaldehyde, nitrogenated compounds, furanone and dicarbonyl type species as well as simple low molecular weight organic acids. Along with methyl glyoxal, the O<sub>2</sub>-bridged ketone and the *m/z* 113 isobaric furanone and  $\delta$ -dicarbonyl ring

15 opening products act as “mass conduits” through which a significant portion of mass transit occurs. Such strong markers could be used during gas phase measurements to “fingerprint” SOA formation episodes in the real atmosphere.

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## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**SOA Formation from  
1,3,5-TMB**

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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ACPD

8, 11685–11754, 2008

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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ACPD

8, 11685–11754, 2008

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





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ACPD

8, 11685–11754, 2008

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



# SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

**Table 1.** Summary of the major gas phase parameters for Experiments 1–7 along with CIR-TOF-MS conditions applied for VOC monitoring.

Exp. No.	Initial [VOC]/ ppbV	Initial [NO]/ ppbV	Initial [NO <sub>b</sub> ]/ ppbV	VOC/NO <sub>x</sub> Ratio	Relative Humidity/%	Exp. Duration <sup>a</sup> / Mins.	Estimated [OH] <sup>b</sup> / pptV	CIR-MS Conditions <sup>c</sup> (E/N)/Td
1	560	129	141	2.07	52	539	0.04	120/170
2	1.180	535	0	2.21	49	521	0.02	120/170
3	143	134	129	0.54	48	596	0.06	140/140
4	554	135	129	2.10	52	521	0.02	120/150
5	151	Continuous HONO input <sup>d</sup>		~15.10	62	488	0.05	90/150
6	597	135	130	2.25	53	462	0.03	90/190
7	166	Continuous HONO input <sup>d</sup>		~16.60	50	549	0.06	90/190

<sup>a</sup> Experiment duration taken from the time that chamber lights were switched on.

<sup>b</sup> Estimated average [OH] over the entire Experiment.

<sup>c</sup> *E/N* conditions of the centre reaction cell/CDC ramping region.

<sup>d</sup> HONO injected continuously throughout experiment, chamber concentration ~10 ppbV.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



# SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

**Table 2.** Summary of the aerosol phase parameter for experiments 1–7.

Exp. No.	CPC Nuc. T <sup>a</sup> /Mins.	SMPS Nuc. T <sup>b</sup> /Mins.	[No.] Half Max. /Mins.	Max. [No.] <sup>c</sup> /#cm-3	Time Max. [No.] /Mins.	[NO] <sup>c</sup> Nucleation/ ppbV	[NO]→0 Time <sup>d</sup> /Mins.	Aerosol Diameter (Time) /nm (Mins.)	Aerosol Mass (Time) /μg m <sup>-3</sup> (Mins.)	SOA Yield /%
1	108	108	183	580	225	16.2	152	387 (357)	47 (465)	1.94
2	145	149	167	1099	228	6.2	152–169 <sup>e</sup>	663 (505)	182 (433)	7.47
3	400	420	543	406	609	1.4	325	155 (618)	2 (621)	0.29
4	188	193	226	491	256	1.2	157	507 (484)	36 (415)	2.29
5	50	58	94	407	163	0.4	— <sup>f</sup>	462 (513)	33 (504)	7.87
6	184	182	218	494	257	1.4	162	484 (487)	31 (358)	1.79
7	22	28	43	2216	76	0.4	— <sup>f</sup>	404 (550)	45 (487)	6.21

<sup>a</sup> Nucleation time obtained using data from CPC (particles of diameter  $\geq 3$  nm).<sup>b</sup> Nucleation time obtained using data from SMPS (particles of diameter  $\geq 15$  nm).<sup>c</sup> Data obtained from SMPS.<sup>d</sup> Defined as the time at which [NO] reaches 2 ppbV.<sup>e</sup> NO analyser off line, [NO] dropped below 2 ppbV during this time.<sup>f</sup> Low NO<sub>x</sub> experiment, [NO] < 1 ppbV throughout Experiment.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

I◀

▶I

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



# SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

**Table 3.** Key TMB, O<sub>3</sub> and NO<sub>2</sub> parameters for Experiments 1–7.

Exp. No.	HC Consumed/ %	Peak d[TMB]/dt /Mins.	Peak [O <sub>3</sub> ] Time /Mins.	Peak [O <sub>3</sub> ] /ppbV	Peak [NO <sub>2</sub> ] Time/Mins.	Peak [NO <sub>2</sub> ] /ppbV
1	89.4	130	278	274.1	103	212.7
2	44.3	120	259	365.2	137	446.2
3	91.5	120	600	199.1	188	187.4
4	63.5	110	287	230.8	104	196.4
5	82.2	–	489	43.8	–	–
6	62.1	110	284	226.3	110	200.9
7	92.5	–	551	58.9	–	–

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

I◀

▶I

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Table 4.** Most major VOC contributors to the gas phase as measured by CIR-TOF-MS. Measured  $m/z$ , approximate peak signal intensity, appearance time and tentative assignments are included. MCM species names are included and can be used for navigation around the MCMv3.1 TMB degradation scheme via the MCM website (<http://mcm.leeds.ac.uk/MCM>).

Measured $m/z$	Peak Signal/ncps	Tentative Assignment Name (MCM designation)/(Fig. 6 identifier)	Mass/Da	Appearance Time/Minutes						
				Exp 1	Exp 2	Exp 3	Exp 4	Exp 5	Exp 6	Exp 7
232.20	200	1,3,5-Trimethyl-4-nitrooxy-6,7-dioxa-bicyclo[3.2.1]oct-2-en-8-ol (TM135BPNO3)/(L)	231.20	120	90	n/m	51	36	51	3
214.15	200	TM135BPNO3 Fragment: MH <sup>+</sup> [− H <sub>2</sub> O]	213.19	96	100	87	81	33	12	27
185.20	300	8-Hydroxy-1,3,5-trimethyl-6,7-dioxa-bicyclo[3.2.1]oct-3-en-2-one (TM135OBPOH)/(P)	184.19	130	130	288 <sup>+</sup>	108	24	60	15
		2-Methyl-3-(1-methyl-3-oxo-but-1-enyl)-oxirane-2-carboxylic acid (TM135MUO2H)	184.19							
169.22	70	1,3,5-Trimethyl-6,7-dioxa-bicyclo[3.2.1]oct-3-ene-2,8-diol (TM135BP2OH)/(O) Fragment: MH <sup>+</sup> [−H <sub>2</sub> O]	169.20	36	93	n/m	69	36	42	3
		2-Methyl-3-(1-methyl-3-oxo-but-1-enyl)-oxirane-2-carbaldehyde (TM135OXMUC)	168.19							
167.18	120	3,5-Dimethyl-benzenecarboxyperoxy acid (TMBCO3H)	166.18	147	177	n/m	81	114	63	n/m
157.20	150	5-Hydroxy-4-methyl-hept-3-ene-2,6-dione (C7M2CO5OH)	156.18	150	126	240	99	102	66	24
155.18	120	4-Methyl-hept-4-ene-2,3,6-trione (C7M3CO)	154.17	453 <sup>+</sup>	171	n/m	111	183	129	30 <sup>+</sup>

n/a = Mass not applicable

n/m = Compound not measured during specific Experiment

\* = Weak signal, appearance time not reported

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Table 4. Continued.

Measured $m/z$	Peak Signal/ncps	Tentative Assignment Name (MCM designation)/(Fig. 6 identifier)	Mass/Da	Appearance Time/Minutes						
				Exp 1	Exp 2	Exp 3	Exp 4	Exp 5	Exp 6	Exp 7
153.22	100	(3,5-Dimethyl-phenyl)-methyl-hydroperoxide (TM-BOOH)	152.20							
151.17	160	3,5-dimethylbenzoic acid (TMBCO <sub>2</sub> H)	150.18	105	84	465*	72	135	60	39*
		2-Methyl-4-oxo-pent-2-enoic acid (C <sub>5</sub> CO <sub>2</sub> BCO <sub>3</sub> H)	144.13							
145.17	50	2-Hydroxy-2-methyl-3,4-dioxo-pentanal (C <sub>6</sub> CO <sub>3</sub> MOH)	144.13							
		2-Oxo-propionic acid 1-methyl-2-oxo-ethyl ester (C <sub>2</sub> CO <sub>3</sub> MCHO)	144.13							
		1-(3-Methyl-3-vinyl-oxiranyl)-ethanone (EPXMALKT)	144.13							
143.19	120	Unidentified	n/a	366*	*	406*	129	78	75	30*
141.18	140	Unidentified	n/a	126	111	*	132	138	75	60
139.18	400	3,5-Dimethyl-phenyl-hydroperoxide (DMPHOOH)	138.16	309*	78	*	51	3	66	3
		2,4,6-trimethyl phenol (TM135BZOL)/(D)	136.19							
137.19	220	(3,5-Dimethyl-phenyl)-methanol (TMBOH)	136.19	81	75	96	54	*	15	15
		m-xyloquinone	136.15							
136.09	400	Unidentified nitrate	n/a	114	132	141	87	45	96	n/m
		3,5-dimethyl benzaldehyde (TMBCHO)/(W)	134.18							
135.18	1000	2-Hydroxy-2-methyl-3-oxo-propaneperoxoic acid (CHOMOHCO <sub>3</sub> H)	134.09	63	78	93	57	30	39	18

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Table 4.** Continued.

Measured <i>m/z</i>	Peak Signal/ncps	Tentative Assignment Name (MCM designation)/(Fig. 6 identifier)	Mass/Da	Appearance Time/Minutes							
				Exp 1	Exp 2	Exp 3	Exp 4	Exp 5	Exp 6	Exp 7	
129.17	500	2-Hydroxy-3-oxo-butaneperoxoic acid (CO2H3CO3H)	134.09								
		Malic acid	134.09								
		2-Methyl-4-oxo-pent-2-enoic acid (C5CODBCO2H)	128.12	84	93	168	66	3	72	33	
		3-Acetyl-2-methyl-oxirane-2-carbaldehyde (EXPMALKT)	128.12								
127.17	300	Related to Bicyclic Signals	n/a	90	90	144	96	99	57	27	
125.15	1200	Bicyclic Fragment: [C <sub>6</sub> H <sub>3</sub> O <sub>3</sub> ]H <sup>+</sup>	125.10	99	102	69	45	3	33	3	
123.17	400	Unidentified	*	*	*	183 <sup>+</sup>	*	*	*	*	
119.18	200	2-Hydroperoxy-2-methyl-malonaldehyde (C3MDIALOOH)	118.09	90	75	*	123	33	69	3 <sup>+</sup>	
117.14	140	Succinic acid	118.09								
		3-Hydroxy-pentane-2,4-dione (C5CO243OH)	116.12	174	129	183	84	42	81	12	
115.13	250	Pentane-2,3,4-trione (C5CO234)	114.10	153	108	183	111	18	3	33 <sup>+</sup>	
113.13	7400	Methyl maleic anhydride (MMALANHY)/(AF)	112.08								
		2-methyl-4-oxo-2-pentenal (C5MDICARB)/(R)	112.13	15	15	33	15	9	3	6	
		3,5-dimethyl-3(2H)-2-furanone/(AF)	112.13								
		3,5-dimethyl-5(2H)-2-furanone (MXFUONE)/(S)	112.13								

ACPD

8, 11685–11754, 2008

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





**Table 4.** Continued.

Measured $m/z$	Peak Signal/ncps	Tentative Assignment Name (MCM designation)/(Fig. 6 identifier)	Mass/Da	Appearance Time/Minutes						
				Exp 1	2	Exp 3	Exp 4	Exp 5	Exp 6	Exp 7
111.12	6000	3 methyl-5-methylidene-5-(2H) furanone	110.04	72	60	105	66	15	21	39
109.15	400	TM135BPNO3 Fragment: $MH^+[-O.NO_3.3(CH_3)]$	109.10	84	75	51	60	3	54	3
103.11	150	2-Hydroxy-2-methyl-malonaldehyde (C3MDIALOH)	102.09	150	126	*	126	93	12	27
101.13	400	2,3-dioxobutanal	100.7	126	90	129	84	60	12	15
99.12	160	Unidentified	n/a	183	171	n/m	177*	366	99	30*
97.13	1000	Unidentified	n/a	72	78	102	81	51	9	33
87.10	1200	Related to Bicyclic Signals	n/a	117	75	123	90	42	12	24
85.11	500	$m/z$ 113 Fragment: $MH^+[-CO]$ Butenedial	85.13 84.07	84	63	81	51	63	33	27
77.07	1400	Hydroxy acetic acid (CH <sub>3</sub> CO <sub>3</sub> H)	76.05	99	135	168	90	36	63	15
75.09	400	Hydroxyacetone	74.08	141	66	147	105	72	66	3
		Oxo-acetic acid (HCOCO <sub>2</sub> H)	74.04							
73.07	1600	Methyl glyoxal (MGLYOX)/(Q)	72.06	36	30	39	15	9	36	15
61.07	6000	Acetic Acid (CH <sub>3</sub> CO <sub>2</sub> H)/(X)	60.05	36	72	60	90	12	18	3
		Glycoaldehyde	60.50							
		Pyruvic Acid Fragment	88.06							
		Lactic Acid Fragment	90.08							

# SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



# SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

**Table 4.** Continued.

Measured $m/z$	Peak Signal/ncps	Tentative Assignment Name (MCM designation)/(Fig. 6 identifier)	Mass/Da	Appearance Time/Minutes						
				Exp 1	Exp 2	Exp 3	Exp 4	Exp 5	Exp 6	Exp 7
59.08	1200	Acetone	58.08	n/m	n/m	174	51	72*	207	27
57.10	1000	Carbonyl/Hydrocarbon Fragment: [C <sub>3</sub> H <sub>5</sub> O <sup>+</sup> ] / [C <sub>4</sub> H <sub>9</sub> <sup>+</sup> ]	57.07 / 57.12	225	141	n/m	147	114	183	51
47.01	600	Formic Acid/(Y)	46.03	198	105	69	72	72	252	*
46.01	5000	PAN Fragment: [NO <sub>2</sub> <sup>+</sup> ]	46.01	102	105	105	72	93	72	51
45.06	3500	Me. Glyoxal Fragment (CH <sub>3</sub> OOH)/(AD)	44.05	63	42	93	48	99	45	12
43.04	5000	Carbonyl/Hydrocarbon Fragment: [C <sub>2</sub> H <sub>3</sub> O <sup>+</sup> ] / [C <sub>3</sub> H <sub>7</sub> <sup>+</sup> ]	43.05 / 43.09	63	18	69	57	3	3	0
33.05	5000	Methanol (CH <sub>3</sub> OH)/(AA)	32.04	105	141	399*	106	132	153	90
31.03	1000	Formaldehyde (HCHO)/(AB)	30.03	264	159	345*	132*	243*	249	27

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Table A1.** CIR-TOF-MS calibration details. The measured compound is given along with the method employed for calibration, the relative humidity of the sample matrix during calibration and, where appropriate the surrogate compound employed. The instrument sensitivity to each given compound is provided along with an uncertainty/error estimate for the measurement.

Target	Method	Relative Humidity/%	Calibration Compound	Sensitivity <sup>a</sup> /ncps ppbV <sup>-1</sup>	Calibration Error <sup>b</sup> /%
2,4,6-trimethyl phenol	Gas Standard <sup>c</sup>	0	Phenol	226.35–372.54	11.04–21.78
3,5-dimethyl benzaldehyde	Gas Standard	0	m-tolualdehyde	98.65–145.35	9.35–17.20
O <sub>2</sub> Bridged Nitrate (TM135BPNO <sub>3</sub> ) <sup>d</sup>	Gas Standard	0	m-tolualdehyde	98.65–145.35	9.35–17.20
O <sub>2</sub> Bridged Diol (TM135BP2OH) <sup>d</sup>	Gas Standard	0	m-tolualdehyde	98.65–145.35	9.35–17.20
O <sub>2</sub> Bridged Ketone (TM135OBPOH) <sup>d</sup>	Gas Standard	0	m-tolualdehyde	98.65–145.35	9.35–17.20
Bicyclic Marker <sup>d</sup>	Gas Standard	0	m-tolualdehyde	98.65–145.35	9.35–17.20
<i>m/z</i> 129	Permeation Tube	50	Methacrolein	9.46–19.27	3.95–4.20
Unsaturated Anhydrides ( <i>m/z</i> 111 & 113)	Teflon Bag <sup>e</sup>	50	Citraconic Anhydride	32.53–119.90	27.60–27.63
Hydroxy Acetic Acid	Permeation Tube <sup>f</sup>	50	Acetic Acid	17.43–45.93	2.93–5.96
Hydroxy Acetone	Permeation Tube	50	Acetone	55.60–104.04	3.25–4.87
Methyl Glyoxal	Permeation Tube	50	Isoprene	9.46–19.27	6.53–11.56
Acetic Acid	Permeation Tube	50	Acetic Acid	17.43–45.93	2.93–5.96
Acetone	Permeation Tube	50	Acetone	55.60–104.04	3.25–4.87
Formic Acid	Permeation Tube	50	Formic Acid	5.14–9.52	3.77–6.78
Acetaldehyde	Permeation Tube	50	Acetaldehyde	57.01–107.33	3.17–3.31
Carbonyl Marker	Permeation Tube	50	Acetone	55.60–104.04	3.25–4.87
Methanol	Permeation Tube	50	Methanol	22.25–46.06	3/94–6.76

<sup>a</sup> Instrument sensitivity is given as a range covering all drift cell conditions employed during the study (see Table 1 for further information).

<sup>b</sup> Measurement uncertainty/error is given as a range covering all drift cell conditions employed during the study (see Table 1 for further information).

<sup>c</sup> Gas standards provided by Air Environmental Inc. (US) and courtesy of PSI. Compound mixing ratio accuracy: 10%.

<sup>d</sup> Calibrated values used only to calculate “pseudo” VOC yields.

<sup>e</sup> Calibration conducted by injecting liquid citraconic anhydride (Sigma Aldrich, 99%) into an 80 L Teflon sample bag (SKC, Ltd). Sticking factors employed to adjust for deposition/wall loss.

<sup>f</sup> Permeation tubes supplied by Ecoscientific (UK) and Vici Inc. (US). Compound emission rate accuracy: 2.02–11.24%.

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Table A2.** VOC yields for various compounds measured by CIR-TOF-MS during Experiments 1–7.

Experiment	Volatile Organic Compound Product Yield / %						
	1	2	3	4	5	6	7
Compound							
O <sub>2</sub> Bridged Nitrate (TM135BPNO3)	1.8	2.8	2.7	2.9	4.3	3.7	5.1
O <sub>2</sub> Bridged Ketone (TM135OBPOH)	0.7	0.6	1.0	1.1	3.0	0.8	2.3
O <sub>2</sub> Bridged Diol (TM13BP2OH)	0.2	0.3	n/m	0.4	0.8	0.2	0.9
3,5-dimethylphenol							
3,5-dimethyl benzaldehyde	1.3	2.5	1.6	2.6	1.9	2.7	2.2
<i>m/z</i> 129	5.0	4.4	11.8	18.6	29.5	8.4	12.9
<i>m/z</i> 113	15.6	46.6	37.2	38.4	33.3	39.6	26.5
3 Me. 5-methyl-5-(2H) furanone	5.7	10.3	8.8	7.9	3.6	8.1	8.9
Hydroxy-acetone	0.6	0.5	1.1	1.0	1.5	0.6	1.2
Hydroxy acetic acid	3.1	n/m	2.0	3.1	18.6	5.9	8.3
Methyl glyoxal	13.5	24.3	31.1	28.8	21.3	22.5	21.0
Acetic acid	19.5	14.7	11.9	10.0	33.1	16.0	32.2
Acetone	n/m	0.4	3.3	1.4	3.1	1.3	1.5
Formic acid	11.51	13.1	32.5	15.3	48.5	10.9	n/m
Carbonyls	32.1	44.7	51.2	26.2	17.8	24.9	41.2
Methanol	1.7	1.0	1.0	0.7	2.8	1.4	2.6

n/m: Not measured

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

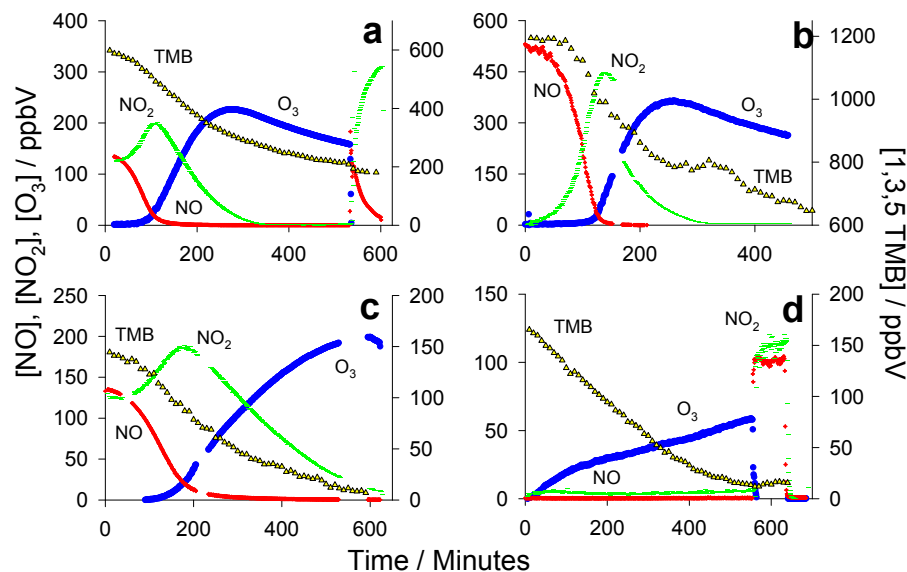
Printer-friendly Version

Interactive Discussion



SOA Formation from  
1,3,5-TMB

K. P. Wyche et al.



**Fig. 1.** Temporal evolution of the major gas phase components of the 1,3,5-TMB photooxidation system during (a) Experiment 6 (VOC/NO<sub>x</sub>~2:1), (b) Experiment 2 (VOC/NO<sub>x</sub>~2:1, NO only), (c) Experiment 3 (VOC/NO<sub>x</sub>~1:2) and (d) Experiment 7 (VOC/NO<sub>x</sub>~17:1). In each plot the left ordinate axis gives the concentration of the inorganic components (NO, NO<sub>2</sub> and O<sub>3</sub>) while the right axis gives the concentration of TMB.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

I◀

▶I

◀

▶

Back

Close

Full Screen / Esc

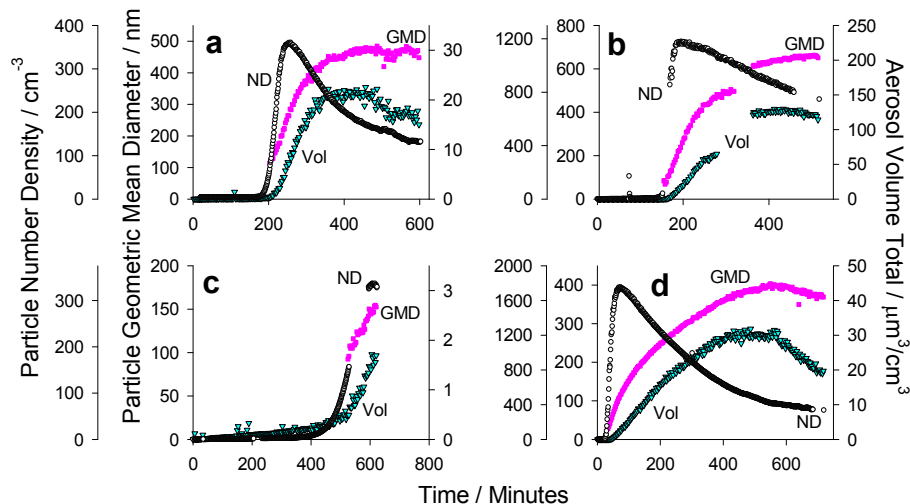
Printer-friendly Version

Interactive Discussion



SOA Formation from  
1,3,5-TMB

K. P. Wyche et al.

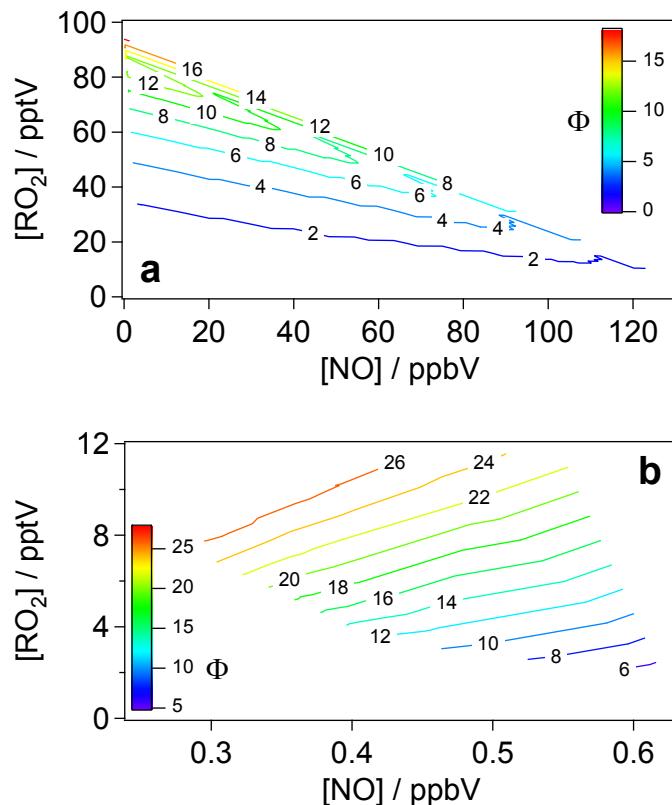


**Fig. 2.** Temporal evolution of the aerosol number density (ND), geometric mean diameter (GMD) and volume concentration (Vol) within the chamber during **(a)** Experiment 6 (VOC/NO<sub>x</sub> ~ 2:1), **(b)** Experiment 2 (VOC/NO<sub>x</sub> ~ 2:1, NO only), **(c)** Experiment 3 (VOC/NO<sub>x</sub> ~ 1:2) and **(d)** Experiment 7 (VOC/NO<sub>x</sub> ~ 17:1).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

**SOA Formation from  
1,3,5-TMB**

K. P. Wyche et al.



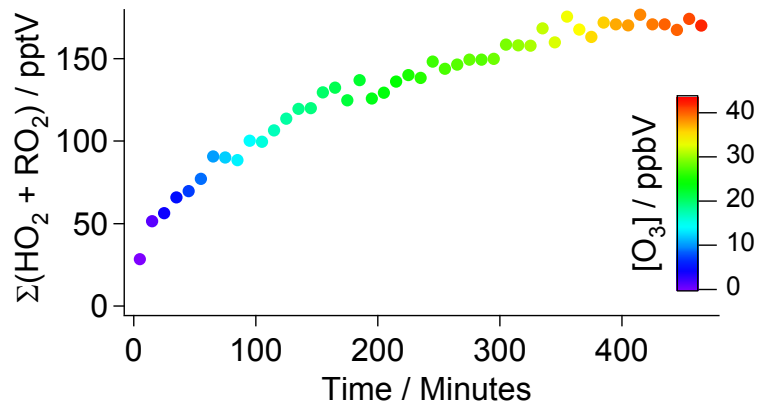
**Fig. 3.** Theoretical variation in partitioning of  $\text{RO}_2$  species with evolving chamber  $[\text{NO}]$  for **(a)** high  $\text{NO}_x$  conditions and **(b)** low  $\text{NO}_x$  conditions.  $\Phi$  gives the percentage of  $\text{RO}_2$  species forming peroxides (see Eq. 2 and text for further details).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)



**SOA Formation from  
1,3,5-TMB**

K. P. Wyche et al.

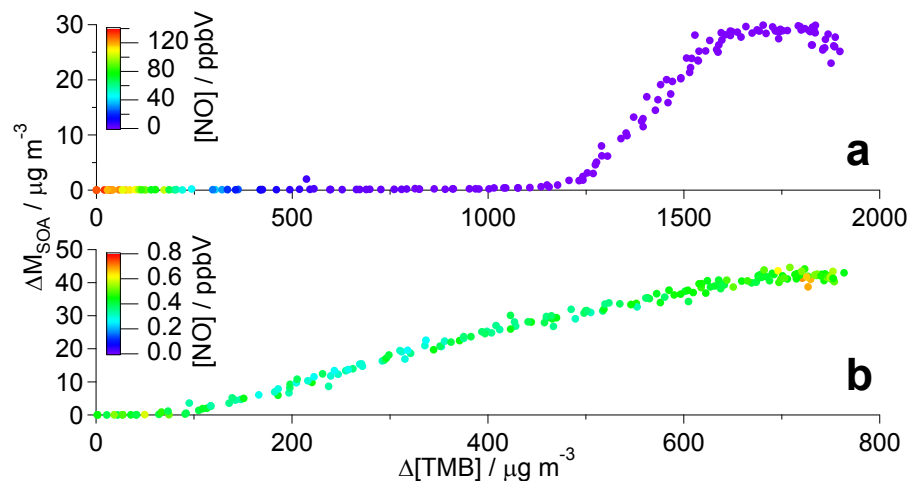


**Fig. 4.** Temporal evolution of the sum of hydro and organic peroxy radicals (i.e.  $\Sigma(\text{HO}_2 + \text{RO}_2)$ ) recorded by the PERCA during the low  $\text{NO}_x$  Experiment 5 (VOC/ $\text{NO}_x$  ratio  $\sim 15:1$ ).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

SOA Formation from  
1,3,5-TMB

K. P. Wyche et al.



**Fig. 5.** SOA growth curves for (a) Experiment 6 (high  $\text{NO}_x$  experiment,  $\text{VOC}/\text{NO}_x \sim 2:1$ ) and (b) Experiment 7 (low  $\text{NO}_x$  experiment,  $\text{VOC}/\text{NO}_x \sim 17:1$ ).  $\Delta[\text{TMB}]$ =reacted mass of TMB following initiation of the oxidation chemistry.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

I◀

▶I

◀

▶

Back

Close

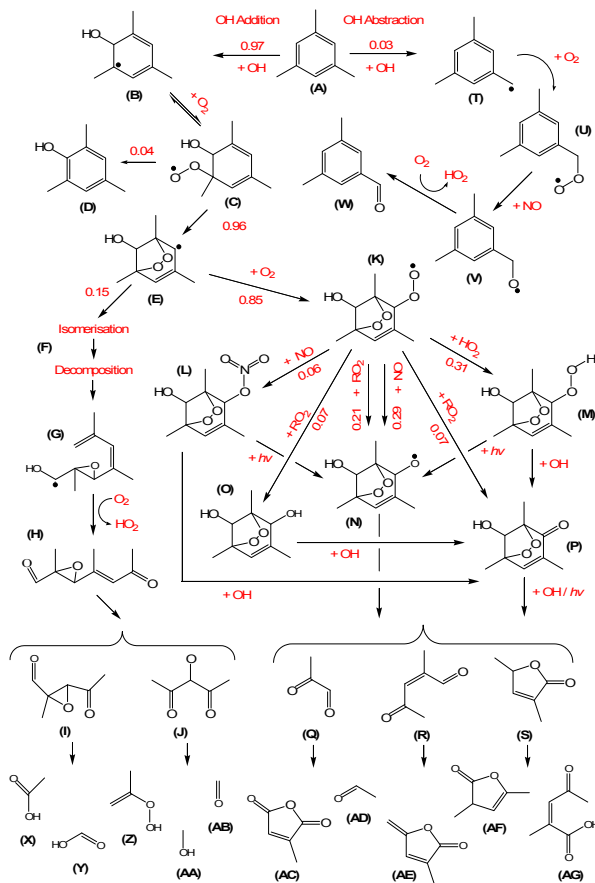
Full Screen / Esc

Printer-friendly Version

Interactive Discussion



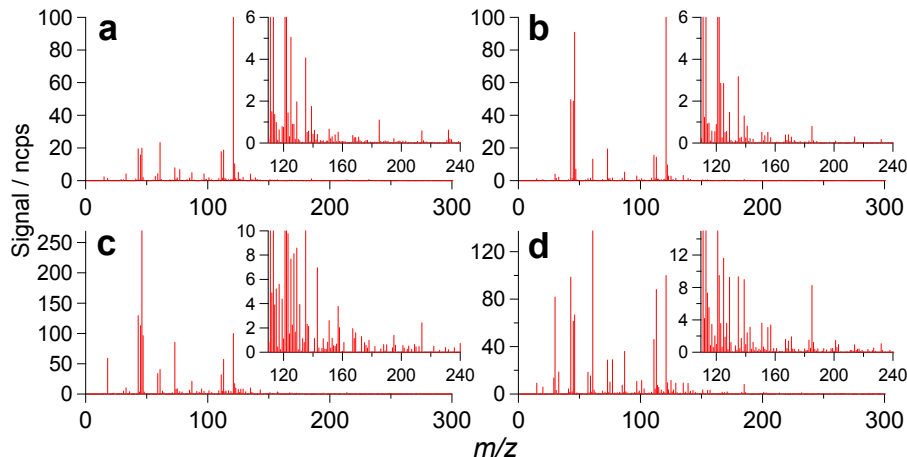
## K. P. Wyche et al.



**Fig. 6.** Mechanism summary of OH radical-induced photooxidation of 1,3,5-trimethylbenzene. Key primary and secondary product formation shown, branching ratios are taken from MCMv3.1 (<http://mcm.leeds.ac.uk/mcm>) (see text).

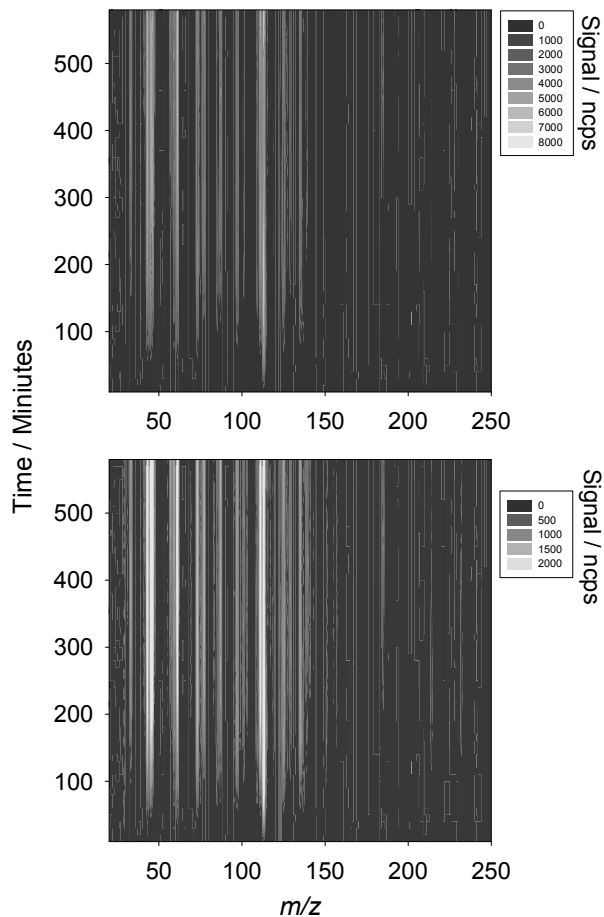
**SOA Formation from  
1,3,5-TMB**

K. P. Wyche et al.



**Fig. 7.** Comparison of CIR-MS mass spectra recorded 400 minutes after the start of experiments for **(a)** Experiment 6 ( $\text{VOC}/\text{NO}_x \sim 2:1$ ), **(b)** Experiment 2 ( $\text{VOC}/\text{NO}_x \sim 2:1$ , NO only), **(c)** Experiment 3 ( $\text{VOC}/\text{NO}_x \sim 1:2$ ) and **(d)** Experiment 7 (low  $\text{NO}_x$ ,  $\text{VOC}/\text{NO}_x \sim 17:1$ ). Each mass spectrum corresponds to data accumulation for a ten-minute period.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)



**Fig. 8.** Evolution of the gas phase organic species during Experiment 6 (VOC/NO<sub>x</sub>~2:1).

## SOA Formation from 1,3,5-TMB

K. P. Wyche et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

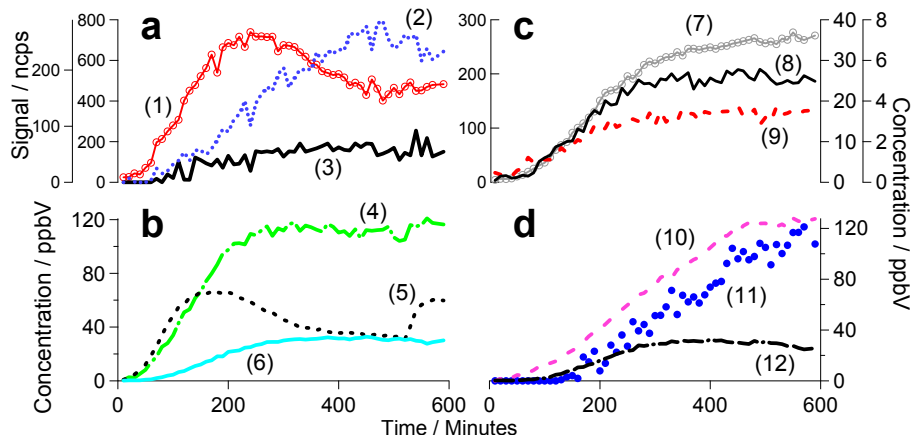
Printer-friendly Version

Interactive Discussion



SOA Formation from  
1,3,5-TMB

K. P. Wyche et al.



**Fig. 9.** Temporal evolution of certain key VOCs during the photooxidation of 1,3,5-TMB in Experiment 6 (VOC/NO<sub>x</sub> 2:1). **(a)** (1) O<sub>2</sub>-bridged nitrate, (2) O<sub>2</sub>-bridged ketone (on right axis), (3) O<sub>2</sub>-bridged diol fragment, **(b)** (4) methyl glyoxal, (5) *m/z* 113-isobaric ring opening products citraconic anhydride, 3,5-dimethyl-3(2H)-2-furanone, 3,5-dimethyl-5(2H)-2-furanone and 2-methyl-4-oxo-2-pentenal,, (6) 3-methyl-5-methylidene-5-(2H)-furanone, **(c)** (7) *m/z* 43: carbonyl marker (left axis), (8) 2-methyl-4-oxo-pent-2-enoic acid and 3-acetyl-2-methyl-oxirane-2-carbaldehyde (first right axis), (9) hydroxy acetone (second right axis) and **(d)** (10) acetic acid, (11) formic acid, (12) hydroxy acetic acid.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

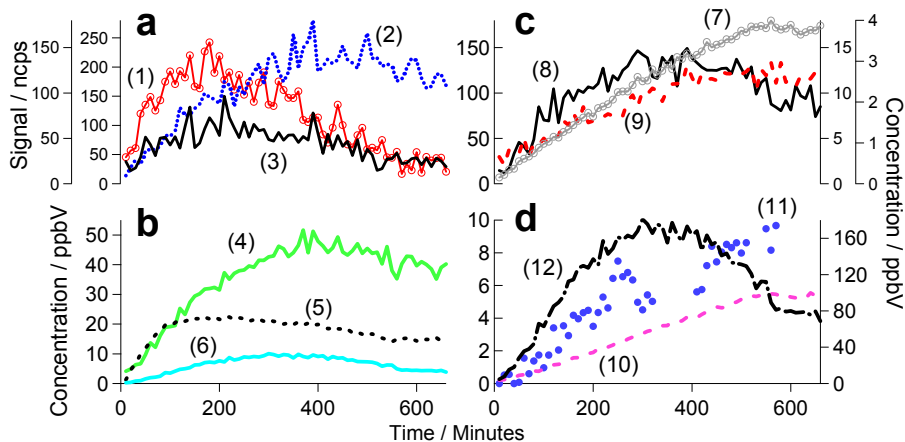
Printer-friendly Version

Interactive Discussion



SOA Formation from  
1,3,5-TMB

K. P. Wyche et al.



**Fig. 10.** Temporal evolution of certain key VOCs during the photooxidation of 1,3,5-TMB during experiment 7 (VOC/NO<sub>x</sub>~17:1). Compound numbering is the same as that used in the caption for Fig. 9. Note: in figure (a) signal of O<sub>2</sub>-bridged diol (3) is given on the right axis and in figure (d) concentration of hydroxyl acetic acid (10) is given on the left axis.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

I◀

▶I

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

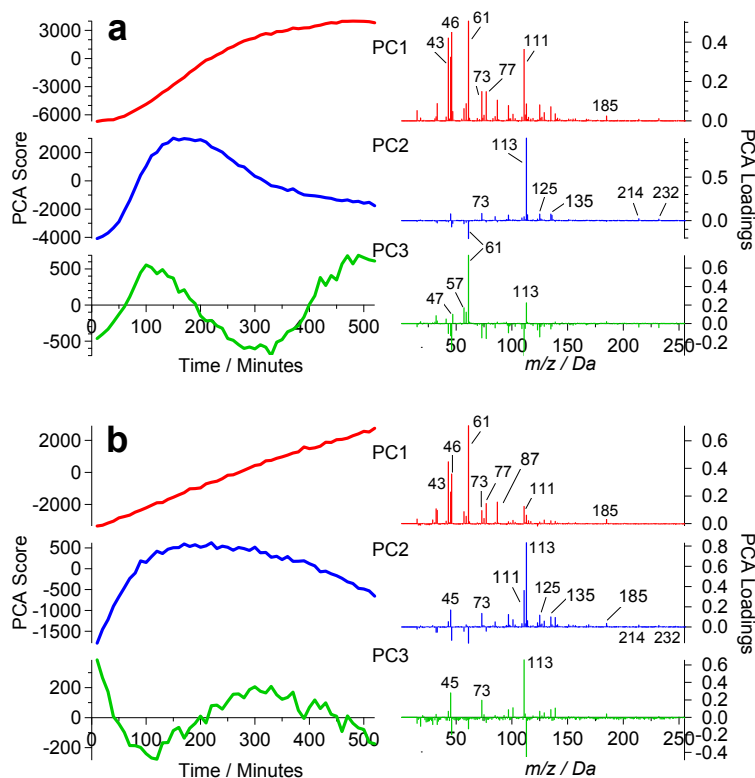
Interactive Discussion





SOA Formation from  
1,3,5-TMB

K. P. Wyche et al.

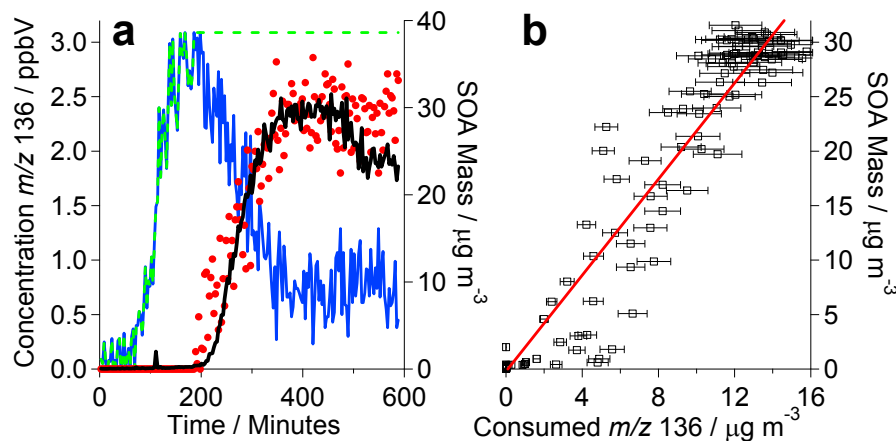


**Fig. 11.** Principal component analysis conducted on VOC data for **(a)** Experiment 6 (high  $\text{NO}_x$ ,  $\text{VOC}/\text{NO}_x \sim 2:1$ ) and **(b)** Experiment 7 (low  $\text{NO}_x$ ,  $\text{VOC}/\text{NO}_x \sim 17:1$ ). Percentage variance captured: PC1=78.0%, PC2=19.7% and PC3=1.9% for Experiment 6 and PC1=90.0%, PC2=8.0% and PC3=0.6% for Experiment 7.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

SOA Formation from  
1,3,5-TMB

K. P. Wyche et al.



**Fig. 12. (a)** Temporal evolution of the unidentified nitrate of  $m/z$  136 (solid blue line) during Experiment 6 (high  $\text{NO}_x$ ). Plot includes total amount of  $m/z$  136 formed (dashed green line) and total amount lost (red circles). Also included is an overlaid profile of SOA mass (solid black line). **(b)** Correlation between  $m/z$  136 mass lost and SOA mass formed (up to the point of peak mass) for Experiment 6. Line fit:  $y = 2.21 (\pm 0.04)x - 0.21 (\pm 0.35)$ ,  $r^2 = 0.94$ . Coefficients quoted  $\pm$  one standard deviation.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

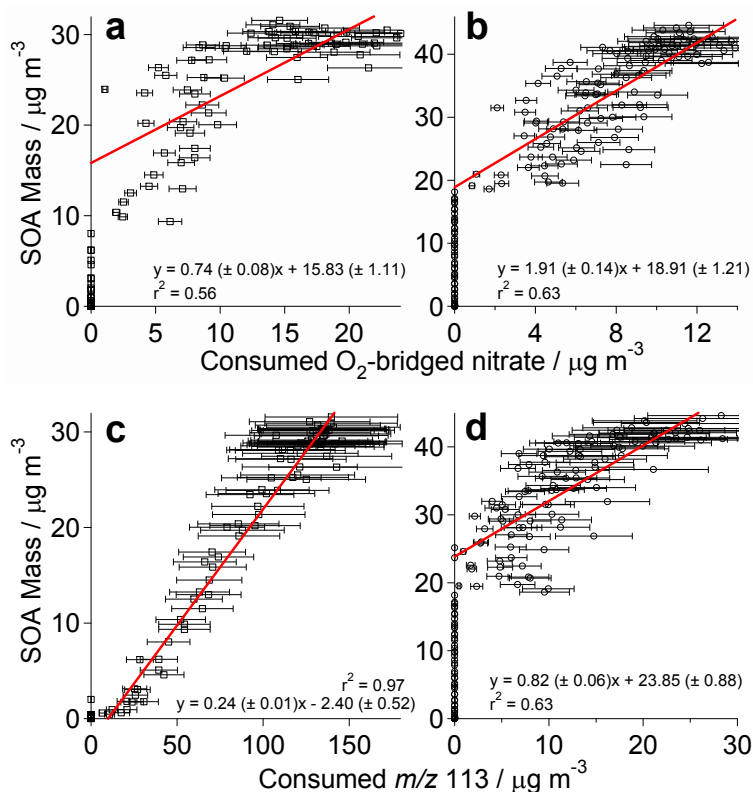
Printer-friendly Version

Interactive Discussion



SOA Formation from  
1,3,5-TMB

K. P. Wyche et al.



**Fig. 13.** Correlation between mass of VOC lost and mass of SOA formed (up to the point of peak mass), for the  $\text{O}_2$ -bridged nitrate for **(a)** Experiment 6 (high  $\text{NO}_x$ ) and **(b)** Experiment 7 (low  $\text{NO}_x$ ) and for the  $m/z$  113 ring opening compounds for **(c)** Experiment 6 and **(d)** Experiment 7. Correlation coefficients quoted  $\pm$  one standard deviation.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)